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# A TRIDENT SCHOLAR PROJECT REPORT

NO. 164

"A Theoretical Study of Conjugation in  
Para-Substituted Nitrobenzenes"



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER U.S.N.A. - TSPR; 164 (1990)	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) A THEORETICAL STUDY OF CONJUGATION IN PARA-SUBSTITUTED NITROBENZENES.		5. TYPE OF REPORT & PERIOD COVERED Final 1989/90
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) James R. Barney		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS United States Naval Academy, Annapolis.		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS United States Naval Academy, Annapolis.		12. REPORT DATE 22 May 1990
		13. NUMBER OF PAGES 84
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  This document has been approved for public release; its distribution is UNLIMITED.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES  Accepted by the U.S. Trident Scholar Committee.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Benzene Chemistry, Physical organic Mesomerism Ring formation (Chemistry)  Hammett equation		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The much-debated electronic structure of para-substituted nitrobenzene is studied by means of fully optimized geometric analysis of variously substituted nitrobenzenes in which the electronic character of the substituents covers a wide range of Hammett $\sigma$ values. The investigation concerns the electronic effects of substituent to ring conjugation on six parameters: barrier to rotation of the $\text{NO}_2$ group, C-N bond length, ring C-C (OVER)		

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bond lengths and substituent to ring bond lengths,  $p(z)$  orbital overlap between the  $\text{NO}_2$  group and the ring, and the charge density on the  $\text{NO}_2$  oxygens. It is theorized that the change in barrier to rotation over the  $\sigma$  spectrum is directly related to the degree of conjugation to the nitro group. The data, gathered from AM1 calculations on the semi-empirical level, show that the hybrid valence bond structure of p-nitrobenzene does receive a significant contribution from an electronic configuration which is stabilized by "through-resonance." Although this contribution may be relatively small, it is not negligible as has been recently suggested. As a means for comparison, the same relationships are studied in meta-substituted nitrobenzenes and para-substituted benzoates, both of which are presumed to receive very minimal contributions from through-resonance stabilized structures, and p-substituted benzaldehydes, which are considered to be substantially resonance stabilized.

S/N 0102-LF-014-6601

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U.S.N.A. - Trident Scholar project report; no. 164 (1990)

**"A Theoretical Study of Conjugation in  
Para-Substituted Nitrobenzenes"**

**A Trident Scholar Project Report**

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## ABSTRACT

The much-debated electronic structure of para-substituted nitrobenzene is studied by means of fully optimized geometric analysis of variously substituted nitrobenzenes in which the electronic character of the substituents covers a wide range of Hammett  $\sigma$  values. The investigation concerns the electronic effects of substituent to ring conjugation on six parameters: barrier to rotation of the NO<sub>2</sub> group, C-N bond length, ring C-C bond lengths and substituent to ring bond lengths, p(z) orbital overlap between the NO<sub>2</sub> group and the ring, and the charge density on the NO<sub>2</sub> oxygens. It is theorized that the change in barrier to rotation over the  $\sigma$  spectrum is directly related to the degree of conjugation to the nitro group. The data, gathered from AM1 calculations on the semi-empirical level, show that the hybrid valence bond structure of p-nitrobenzene does receive a significant contribution from an electronic configuration which is stabilized by "through-resonance." Although this contribution may be relatively small, it is not negligible as has been recently suggested. As a means for comparison, the same relationships are studied in meta-substituted nitrobenzenes and para-substituted benzoates, both of which are presumed to receive very minimal contributions from through-resonance stabilized structures, and p-substituted

benzaldehydes, which are considered to be substantially resonance stabilized.

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## I. INTRODUCTION

### A. Electronic Structure of Substituted Benzenes

In the past twenty years there has been considerable debate over the electronic structure of substituted and disubstituted benzene compounds. One aspect in particular that has received much attention is the concept of "through-resonance" in 1,4 disubstituted benzenes.<sup>1,2,3,4,5</sup> With through-resonance, the  $\pi$  electron withdrawing effects of functional groups such as CHO and COR are satiated by coupling (via conjugated  $\pi$  bonds) to an electron donating substituent (or visa versa). The effect is usually described in terms of valence bond theory with the overall electronic structure of the molecule being a "hybrid" made up of several substituent isomers each with a specific valence bond configuration. Perhaps a more direct way to describe through-resonance is that the increase in  $\pi$  orbital overlap which occurs allows electron delocalization which thereby extends the  $\pi$  electron communication to and from the ring. The overall effect of the increased communication is a reduction in energy. The 1,4 disubstituted benzenes are thus stabilized by through-resonance.

## B. Lipkowitz's Analysis of Substituted Nitrobenzenes

Para-substituted nitrobenzene (Figure 1) has long been thought to be a prime example of resonance stabilization in conjugated ring systems.<sup>1</sup> However, in the past 10 years, this idea has been contradicted in several papers.<sup>1,3,4,5</sup> Several of these papers were based on information gathered from <sup>17</sup>O NMR shifts. Since these shifts reflect the relative charge density on the oxygen atoms of the nitro group, they are a good measure of the electronic effect a given substituent has on the nitro group.<sup>1,2,3</sup> In 1982, Lipkowitz reported that <sup>17</sup>O NMR shifts indicated very little change in the nitro oxygen electron density over a wide range of para substituents.<sup>3</sup> From this he theorized that ". . . the nitro group withdraws a constant amount of electron density from the ring regardless of what substituent is attached to the meta or para position." Lipkowitz used valence bond hybrid structures to illustrate the electronic conformations available to para-substituted nitrobenzenes (Figures 2 and 3). He proposed that since the electron density of nitro oxygens is independent of the  $\pi$  electron donating ability of the para or meta substituents, then conjugated resonance structures (2e and 3c) do not play a major role in the total electronic make-up of nitrobenzene as is commonly thought. As a comparison to nitrobenzenes, Lipkowitz also investigated the nitro oxygen charge density relationships of benzophenones, benzaldehydes, and

acetophenones, all of which are assumed to be resonance stabilized. He found that all three compounds exhibit strong correlations between  $^{17}\text{O}$  NMR shifts and the  $\pi$  electron donating ability of the substituents. Lipkowitz proposed a valence bond structure for para-substituted nitrobenzenes that does not result in the loss of nitro resonance (Figure 2a). In such a resonance hybrid, the nitro oxygens would be shielded from the effects of para and meta substituents. In effect, the aromatic ring and nitro groups form two independent, delocalized systems.

#### C. Other Analyses of Substituted Nitrobenzenes

In 1983, Fraser, Ragauskas and Stothers reported  $^{17}\text{O}$  NMR data that totally contradicted Lipkowitz's findings.<sup>2</sup> They stated that Lipkowitz's conclusion ". . . if correct, would have far reaching consequences because it refutes current concepts of valence bond theory of resonance and would require a complete revision of all standard textbooks of organic chemistry." They refuted this conclusion based on an experimental method nearly identical to that used by Lipkowitz except with a wider range of substituents and a better resolution of spectra. They concluded that  $^{17}\text{O}$  NMR shifts were strongly related to the electron donating ability of the para substituent ". . . in a manner completely consistent with existing valence bond theory."

In 1984, Hiberty and Ohanessian concluded, based on

theoretical methods, that both reports were partly correct in their conclusions.<sup>1</sup> Using theoretical modeling on two compounds, nitrophenol and nitroaniline, both with experimental geometries, Hiberty and Ohanessian showed that Lipkowitz's findings were substantiated by a 5 to 7 fold predominance of Structure 2c and 2d over 2e. However, they also noted that there is some degree of resonance that, under the proper conditions, could lead to a significant <sup>17</sup>O NMR shift as reported by Fraser, Ragauskas and Stothers. They estimated that Structure 2e accounts for 1% to 11% of the overall electronic structure.

In 1987 Politzer, Lane, Dayasuriya and Domelsmith<sup>6</sup> reported that an analysis of the electrostatic potentials of unsubstituted nitrobenzene, both with the NO<sub>2</sub> group planar and orthogonal, indicated that Lipkowitz's conclusion was valid. They stated that their results were ". . . indicative of a very minor degree of conjugation between the nitro group and the aromatic ring of nitrobenzene." They suggested that property changes accompanying the rotation of the NO<sub>2</sub> group out of the plane of the ring may be the result of rearrangements in electron density but not necessarily indicative of changes in conjugation.

#### D. Hammett $\sigma$ Values

All of the aforementioned investigations employed methods that centered around the "electron donating

ability" of the various substituents. Thus, there must be some standard scale by which these values can be determined. This scale is derived from the Hammett equation and is based on the assumption that electron transfer in conjugated systems represents a Linear Free Energy Relationship.<sup>7,8</sup> Hammett found that fluctuation in the electron density of a carboxyl group para or meta to a substituent manifests itself in changes in acidity. He used the  $K_a$  values of unsubstituted benzoic acid as a standard by which to measure the effect of a given substituent. For instance, if an  $\text{NH}_2$  group is added para to the carboxylic acid group, it becomes less acidic, whereas an  $\text{NO}_2$  group in that position causes the acid to become more acidic. This type of treatment led to the development of  $\sigma$  values which quantify the overall electron donating effect of any substituent. The para hydrogen on benzoic acid was defined as having a  $\sigma$  value of 0. Thus, any substituent more electron donating than H will have  $\sigma$  values less than zero while those substituents that are better electron withdrawing groups than H will have positive  $\sigma$  values. Over the years, these values have been accurately refined. In addition they have been divided into, among other things,  $\sigma_{(I)}$  and  $\sigma_{(R)}$  values which represent the relative contribution to the inductive and resonance effects respectively.<sup>8</sup>

## II. APPROACH

### A. Overview

The approach we have taken is theoretical in nature. It differs from that of Hiberty and Ohanessian in that it investigates the nature of several parameters that are affected by the electron donating effect of the para substituent. Among these is the barrier to rotation of the NO<sub>2</sub> group as it rotates 90 degrees out of the plane of the ring. We propose that this barrier to rotation (BTR) is directly related to the  $\pi$  character of the C-N bond and that this is indicative of resonance. When the NO<sub>2</sub> group is in the orthogonal position, the p orbitals that are responsible for  $\pi$  bonding between the ring and the group are also orthogonal to each other thereby prohibiting  $\pi$  bonding. Because no  $\pi$  orbital overlap can occur with the ring  $\pi$  system while the NO<sub>2</sub> group is orthogonal to the ring, we may assume that the energy difference between the planar and the orthogonal configuration is proportional to the amount of  $\pi$  bonding character present in the planar conformation. Several other parameters will also be investigated to substantiate the BTR relationships. Our approach also differs from their approach in that all geometries were allowed to fully optimize. The point group symmetry of the molecule was maintained and the benzene ring was constrained to be planar,<sup>8,9,10,11</sup> but all other bond lengths and bond angles were allowed to vary.

Atom positions for both the nitrobenzenes and benzoates are given in Figure 1. Because we are studying nitrobenzene as a fully optimized system, we must consider that any parameter will be affected by quite a number of interrelated forces and effects which can never be fully separated. For instance, although the  $\pi$  electron donating ability of a substituent may directly determine the degree of resonance experienced by the nitro group, the inductive effect of that substituent may be such that resonance is in some way hindered or further facilitated. For this reason, we have primarily used  $\sigma$  values rather than  $\sigma_{(R)}$  values. Although this approach tends to make the method less direct, it avoids the pitfalls of assuming certain geometries or certain electronic behavior in a molecule. We will circumvent the problem of having many interrelated effects by analyzing a large number of varying parameters for the system so that we may pinpoint specific, direct relationships.

#### B. Geometric Optimizations

Full geometric optimizations were carried out using the Gaussian 86 program<sup>20</sup> with the AM1 semi-empirical method. Selected values obtained from these optimizations are presented in Tables 1-16. Because of the very large number of optimizations needed for this investigation, ab initio level calculations were not practical. However, the important aspect of our approach, since it deals with

geometric trends, is that all optimizations be carried out consistently and relative to a single set of parameters. Thus, the absolute values obtained from the optimizations may differ slightly from observed values, but the calculated trends should be the same.

In agreement with several previous reports, we have found that the AM1 method provides excellent correlation with experimental geometries<sup>13,14,15,16</sup> and BTRs.<sup>6,10</sup> Whereas ab initio optimizations have yielded BTRs as high as 35.5 kJ/mol for the NO<sub>2</sub> group about the C-N bond in nitrobenzene<sup>6</sup>, our value of 14.53 kJ/mol is in much better agreement with observed values which range from 11.72 kJ/mol to 13.81 kJ/mol.<sup>6,18</sup> In addition, all calculated bond lengths are well within 0.01 Å of observed values. As a point of procedure, we have also confirmed Davis and Guidry's findings that MNDO optimizations fail to predict the planarity of the nitro group with the ring. The BTR obtained for nitrobenzene using MNDO is 7.87 kJ/mol with the 90 degree conformer being the lower in energy.

### III. RESULTS AND DISCUSSION

#### A. Barrier to Rotation

The barrier to rotation of the nitro group in substituted nitrobenzenes should depend on the degree of  $\pi$  bonding between the nitro group and the ring. However,

because a number of parameters might affect this barrier to rotation in addition to  $\pi$  bonding, very little information can be derived from the BTR data of just one compound. We propose, though, that the relationship between BTR and  $\sigma$  values is very indicative of the amount of through-resonance stabilization in substituted nitrobenzene compounds. Thus, a relationship in which the barrier to rotation remains small and constant over a wide range of para substituents will tend to support the theory that Structure 2e is not a major component in the overall electronic configuration of nitrobenzenes. Conversely, a significant correlation between the BTR and the  $\sigma$  values of the substituents will be indicative of a significant contribution from Structure 2e to the overall electronic structure of p-substituted nitrobenzenes.

To ensure that the 0 and 90 degree conformers indeed represent the energy minimum and maximum respectively, a full scale BTR analysis was conducted on p-nitrophenol. Para nitrophenol was used as a typical example of all the substituted nitrobenzene compounds that were studied because of the large amount of literature available on it. It can be seen from Figure 6 that the assumption was correct, with p-nitrophenol having a BTR of 15.47 kJ/mol from the 0 to 90 degree conformer.

The BTR vs.  $\sigma$  relationship that was discussed earlier is shown in Figure 7a. There is a definite correlation evident between the electron donating ability of the

substituents ( $\sigma$  value) and the resulting BTR. Thus, there is undoubtedly some degree of resonance occurring in these molecules, and this resonance increases as the electron donating ability of the substituents increases ( $\sigma$  values become more negative). Bromo, iodo, thiomethyl, and thiol nitrobenzenes are included in the relationship. It should be noted however that the AM1 method may not quite fully optimize compounds containing bromine, iodine, and sulfur since parameters for these atoms are from MNDO and not AM1. Nonetheless, the values obtained for these compounds appear to be in good agreement with the overall observed trends.

Qualitatively, the resonance relationship indicated by Figure 7a is what is predicted by traditional resonance theory. Since  $\text{NO}_2$  is a strong electron withdrawing group, electron donating substituents such as  $\text{NH}_2$  are expected to contribute electron density into the ring via resonance (Structures 2c-2d) and the nitro group readily accepts this electron density via through-resonance (Structure 2e). Resonance is not as favorable however for electron withdrawing groups such as cyano because they induce a net positive charge in the ring (Structures 3a and 3b) which cannot be stabilized by  $\pi$  communication with the  $\text{NO}_2$  group as it is an electron withdrawing group itself. This accounts for the observed decrease in BTR (decrease in  $\pi$  bond character) as  $\sigma$  values increase. In fact, if the electron withdrawing and electron donating sides of the BTR vs.  $\sigma$  relationship are considered independently (Figure 7b)

there is almost a 2.5 fold decrease in the rate at which the BTR decreases relative to  $\sigma$  values on the electron withdrawing side. This is very indicative of a lack of Structure 3c in para-substituted nitrobenzenes.

Now that it has been determined that there is some degree of resonance in para-substituted nitrobenzenes, the question becomes how much? One way to determine this is by comparing the BTR vs.  $\sigma$  relationship of nitrobenzene to those of other disubstituted benzenes. As mentioned before, a number of other parameters could feasibly affect the BTR of the nitro group such as steric hindrance caused by atomic interactions or the orthogonal  $\pi$  orbitals of the ring carbons. Because of this a direct comparison of two dissimilar molecules will be qualitative at best.

Para-substituted benzoates provide a good comparison because the  $\text{COO}^-$  group is isoelectronic with the  $\text{NO}_2$  group and because the two molecules differ structurally by only one atom. When Hammett chose substituted benzoic acid as a reference data set for all  $\sigma$  values, he assumed the benzoate ion to be free from the effects of resonance stabilization.<sup>7</sup> He later noted that resonance caused deviations from the Hammett equation and in fact cited nitrophenols as a specific example. The BTR vs.  $\sigma$  relationship shown in Figure 8 confirms Hammett's assumption that resonance stabilized structures do not contribute much to the overall structure of substituted benzoates. First, the BTRs are considerably smaller than

those for nitrobenzenes. This by itself is not really conclusive, but the fact that the correlation between the BTR of the  $\text{COO}^-$  group about the C1-C7 bond and  $\sigma$  values is approximately half that of the para-substituted nitrobenzenes definitely indicates less resonance in the benzoates.

Finally, it can be seen from Figure 8 that BTRs are decreasing as the substituents become more electron withdrawing. This indicates that although the  $\text{COO}^-$  group has a negative charge, it is not acting as an electron donor. If it were releasing electron density into the ring, the opposite trend of BTR vs.  $\sigma$  would have been observed. The BTR would increase as the substituents became more electron donating. The  $\sigma$  value traditionally assigned to the  $\text{COO}^-$  group is 0;<sup>19</sup> however, the relationship observed in Figure 8 does not support this. A Hammett  $\sigma$  value of 0 indicates that a group has no desire to gain or release electron density from the ring. If this were actually the case for the  $\text{COO}^-$  group, the BTR vs.  $\sigma$  relationship for benzoates would either remain flat or would slope on both sides towards a BTR maximum or minimum at  $\sigma=0$ . Instead, the trend continues linearly through  $\sigma = 0$  towards a minimum at  $\sigma > 0$ . It would seem, then, that the  $\text{COO}^-$  group is actually a very suppressed electron acceptor rather than an electron donor.

Another useful comparison of BTR relationships is that of meta-substituted nitrobenzenes. The geometry of meta

substituted nitrobenzenes does not favor through-resonance. The lack of through-resonance can be seen as a result of the formation of highly charge separated structures such as shown in Figure 4. Because of this, we expect to see very little change in the BTR over the spectrum of  $\sigma$  values as was the case for benzoates. Figure 9 shows the BTR vs.  $\sigma$  relationship for meta-substituted compounds. Note that  $\sigma$  values for substituents in the meta position are different than the corresponding para position values. The results are roughly what is expected. The most important aspect of this relationship is that it represents nearly a four-fold decrease in slope over the para-substituted nitrobenzene BTR vs  $\sigma$  relationship. This provides very conclusive evidence that there is indeed a significant amount of through-resonance occurring in para-substituted nitrobenzenes. A comparison of Figure 9 to Figure 7a reveals that the average meta BTR is about 25% less than the average para BTR. Because meta-substituted and para-substituted nitrobenzenes are structurally nearly the same, this decrease in BTRs may be attributed largely to electronic effects.

It can be seen in Figure 9 that m-methoxynitrobenzene is a bit of an anomaly in the overall trend. This may be explained by the fact that in the AM1 calculations for that compound, the torsion angles of the methyl hydrogens were constrained in a particular geometry rather than being allowed to vary. This may have resulted in slightly higher

calculated  $\Delta H_f$  values for these compounds, though the geometries still correlated quite well with expected values.

Para-substituted benzaldehydes are known to undergo through-resonance stabilization.<sup>3</sup> For this reason, they provide a good comparison to nitrobenzene compounds. Again, because the benzaldehyde structure differs from that of nitrobenzene it is not possible to precisely compare the two quantitatively. However, in qualitative terms it can be said that both compounds experience roughly the same amount of steric hindrance as a result of the interactions between the functional groups and the orthogonal  $\pi$  orbitals of the ring. Thus, it can be assumed that BTRs are equally representative of through-resonance conjugation in both compounds.

A comparison of the BTR vs  $\sigma$  relationships of p-substituted benzoates, benzaldehydes and nitrobenzenes elucidates the extent to which through-resonance occurs in each compound. As mentioned before benzoates are known to undergo very little resonance; the slope of that relationship, shown in Figure 8, is  $-1.83 \text{ kJ/mole}\sigma$ . Benzaldehydes are known to be resonance stabilized, and the slope of that relationship, shown in Figure 10, is  $-4.75 \text{ kJ/mole}\sigma$ . If the assumption is made that the benzoate relationship is indicative of a lack of through-resonance and the benzaldehyde relationship is indicative of a high degree of resonance, a comparison can be made with

nitrobenzenes. The slope of the BTR vs  $\sigma$  relationship of p-substituted nitrobenzenes is -3.74 kJ/mole, which is about twice that of benzoates and nearly equal to the magnitude of the BTR vs.  $\sigma$  relationship of benzaldehydes. Thus, this comparison indicates that nitrobenzenes receive nearly as much contribution from resonance stabilized structures as do benzaldehydes. It must be emphasized that this comparison was not merely based on the relative magnitudes of the BTRs but rather on the relative effects of substituent electron donating ability on the BTRs. As discussed earlier this relationship is more directly reflective of through-resonance conjugation in these compounds.

#### B. Carbon-Nitrogen Bond

Politzer, et. al., reported that the C-N bond length of nitrobenzenes typically increased by 0.01 Å as the molecule changed from the planar to the orthogonal conformer and stated that this change is indicative of a small contribution from Structure 2e.<sup>6</sup> We disagree with the latter assumption on the grounds that when only one substituent is considered, a change in C-N bond distance may be due to some other effect entirely unrelated to resonance. The increase in bond length could be the result, for instance, of increased steric hindrance in the

90 degree conformer arising from the interaction of the orthogonal  $\pi$  orbitals of the ring carbons and the two oxygens in the nitro group.

We propose that the contribution from Structure 2e is best indicated by the change in C-N bond distance over the entire range of  $\sigma$  values. If one assumes that hindrance remains relatively constant over this range, any significant correlation between the bond distance and  $\sigma$  must be due to the electronic effects of the substituents. It can be seen from Figure 11 that this relationship does exist and that the C-N bond distance in both conformers increases steadily as  $\sigma$  values increase. As the substituents become more electron donating, the  $\sigma$  electron density in the ring increases. Sigma electron density in the C-N bond also increases and thus, the C-N bond length decreases somewhat. This effect takes place in both the 0 and the 90 degree conformers; therefore, the only true indicator of the presence of  $\pi$  bonding in the planar conformer is the systematic difference between the C-N bonds of the 0 and 90 degree conformer over a wide range of  $\sigma$  values. This relationship is shown in Figure 12, and it can be seen that there is definitely a linear trend. It is thus apparent that  $\pi$  resonance is occurring in these para-substituted nitrobenzene compounds and that this resonance increases as the substituents become more electron donating. Again, it can be seen that the slopes on either side of  $\sigma = 0$  are different. This is because

with the nitro group being a strong electron withdrawing group, through-resonance is more likely to occur with electron donating substituents than with electron withdrawing substituents.

The C-N bond distance vs.  $\sigma$  relationship of meta substituted nitrobenzenes provides a very important comparison. Since no resonance is likely in these molecules, the change in C-N bond distance over the spectrum of  $\sigma$  values is expected to be very slight. This prediction is manifested in Figure 13. Although there is a change in the C-N bond distances as each molecule goes from the 0 to 90 degree conformer, there is very little change with respect to  $\sigma$ . This fact substantiates the assumption that the hindrance effect remains relatively constant over the range of  $\sigma$  values. The steric hindrance in the meta-substituted nitrobenzenes seems to have about the same effect as it does in para-substituted nitrobenzenes: a systematic 0.01 Å increase in C-N bond length. Figure 14 shows the change in C-N bond length from the 0 to 90 degree conformer vs.  $\sigma$  and as expected the slope is nearly zero.

As with the meta-substituted nitrobenzenes, para-substituted benzoates provide a good comparison with para-substituted nitrobenzenes because there is little resonance stabilization observed in benzoate compounds.<sup>7,8</sup> The relationship seen in Figure 15 substantiates this somewhat in that the change in C1-C7 bond distance over the entire spectrum of  $\sigma$  values is small, only 0.01 Å. As with the

BTR relationship, the direction of the slope shown in Figure 16 for the difference in C1-C7 bond distance vs.  $\sigma$  indicates that COO<sup>-</sup> is acting as a weak withdrawing group rather than an electron donating group.

Once again, p-substituted benzaldehydes may be used as a comparison since they are known to exhibit resonance stabilization. Figure 17 depicts the C1-C7 bond distance vs.  $\sigma$  relationship. As expected, this bond length decreases in both conformers as  $\sigma$  values become more negative. It can be seen that the 0 degree conformer C1-C7 bond decreases more rapidly than does the 90 degree conformer bond because it is affected by both induction and conjugation. The difference between these two slopes is shown in Figure 18, and as can be seen there is a distinct linear relationship.

By comparing the four sets of data, that of p-substituted nitrobenzenes, benzoates and benzaldehydes and m-substituted nitrobenzenes, the relative amount of through-resonance in p-substituted nitrobenzenes can be determined. m-substituted nitrobenzenes do not undergo resonance stabilization, so as expected the difference in C-N bond length vs.  $\sigma$  relationship is nearly 0 (Figure 14). Similar results can be seen for p-substituted benzoates (Figure 16), which receive only a minor contribution from through-resonance stabilization. On the other hand, p-substituted benzaldehydes do undergo resonance stabilization and this leads to the relationship observed

in Figure 18 which has a large slope. The difference in C-N bond distance vs.  $\sigma$  relationship for p-substituted nitrobenzenes shown in Figure 12 has a larger slope than that for benzaldehydes. This supports the contention that there is a significant contribution from resonance stabilized structures in these compounds. No direct quantitative information can be drawn because the bonds that are being compared are not identical; one is a C-N bond whereas the other is a C-C bond. Qualitatively speaking, however, there is no doubt that the relatively large slope seen in Figure 12 is the result of significant ring-to-NO<sub>2</sub> group conjugation.

#### C. Aromatic Carbon-Carbon Bond

Another parameter that is expected to change systematically as the contribution from Structure 2e increases is the C-C bonds in the benzene ring. As the  $\pi$  electron donating ability of the substituent increases the delocalized  $\pi$  electron density in the ring will increase proportionally. Thus, all of the C-C bonds should decrease. However, as Structure 2e becomes more prevalent in the overall structure, the C2-C3 bond should decrease even more while the C3-C4 bond should begin to increase.

Figure 19 shows the relationship of the C2-C3 bond vs.  $\sigma$ . The difference in bond length between the 0 and 90 degree conformers of each molecule is very small (less than

.005A) but it may indicate some degree of resonance stabilization in the planar conformer. More importantly, however, there is a definite trend in the bond length as  $\sigma$  varies. As expected, the bond length decreases in the  $\sigma < 0$  range as the electron donating ability of the substituents increases. As in the BTR relationship, there is a pronounced change of slope as the  $\sigma$  values turn from negative to positive because the electron withdrawing nature of the  $\text{NO}_2$  group inhibits through-resonance with electron withdrawing substituents. Figure 20 shows the relationship of the C3-C4 bond distance vs.  $\sigma$ . Because the C3-C4 bond loses  $\pi$  character as the contribution of Structure 2e increases, the opposite trend is observed than for the C2-C3 bond.

The change in both the C2-C3 and the C3-C4 bond from the planar to the orthogonal conformer with respect to  $\sigma$  values is shown in Figure 21. In this plot it is very easy to see the resonance induced relationships of the aromatic C-C bonds. Another important aspect of this plot is that the two trends continue steadily through the  $\sigma = 0$  point and into the  $\sigma > 0$  region, eventually approaching a value of 0. This indicates that the trend is truly a reflection of through-resonance (Structure 2e) and not just substituent to ring conjugation (Structures 2c-2d and 3a-3b). The latter structures would also have the same effect on the two C-C bonds, but if they were to do so, a "bounce back"

would be observed in the  $\sigma > 0$  region as Structures 3a-3b began to dominate.

Once again, the analogous relationship in meta-substituted nitrobenzenes provides a good comparison since it does not undergo through-resonance stabilization. First, considering the substituent effect on the C2-C3 bond length, it is expected that this bond should increase in length both for  $\sigma < 0$  and  $\sigma > 0$  values. The reason for this is that since the communication between the nitro group and the ring is negligible, there is no suppression of substituent to ring resonance for electron withdrawing groups as there is in para-substituted nitrobenzenes. Thus, on both sides of the  $\sigma$  spectrum, substituent to ring  $\pi$  bonds may be formed, forcing the electronic structure into a hybrid containing Structures 5c-5e. As the strength of this  $\pi$  bonding increases, the contribution of Structure 5a decreases and therefore the C2-C3 bond length increases. From Figure 22 one can see that this prediction is borne out. One anomaly that is obvious, however, is 1,3 dinitrobenzene. The decrease in C2-C3 bond length may result from the balance of the electronic effects of the two nitro groups and increased predominance of Structure 5a. As expected, the opposite trend is seen for the effect of  $\sigma$  values on the C3-C4 bond length in m-substituted nitrobenzenes. This relationship is shown in Figure 23.

The plot of the difference in C2-C3 and C3-C4 bond lengths vs.  $\sigma$  in meta-substituted nitrobenzenes shown in

Figure 24 indicates very clearly the lack of resonance stabilization in these compounds. There is barely any correlation between the differences in bond length and the  $\sigma$  value of the meta substituent, especially when compared to the significant trends observed for para-substituted nitrobenzenes. The difference in C2-C3 and C3-C4 bond lengths vs.  $\sigma$  relationship for p-substituted benzoates is shown in Figure 25. The trends seen here are more slight than those seen for p-substituted nitrobenzenes, indicative of a slight contribution from resonance stabilization. Finally, the analogous relationship for p-substituted benzaldehydes is shown in Figure 26. The trends are virtually identical to those seen for p-substituted nitrobenzenes. The magnitudes of the slopes are nearly the same thus indicating that roughly the same degree of resonance-stabilization occurs in both types of compounds.

#### D. Substituent to Ring Bond

Another parameter that is pertinent to this study is the substituent to ring (C-X) bond. As the substituent resonates with the ring, whether it be full through-resonance or simple substituent to ring resonance (Structures 2c-2d), the increased  $\pi$  density that builds up between the substituent and the ring causes a shortening of the C-X bond. Thus, for para-substituted nitrobenzenes, which have thus far been shown to undergo some degree of resonance, we expect to see an increase in the C-X bond

distance as the nitro group rotates 90 degrees out of the plane of the ring because of a loss of resonance. In addition, because resonance will be enhanced by electron donating substituents, we expect to see an increase in this bond length difference as  $\sigma$  values become more negative. As can be seen in Figure 20, this trend is readily apparent. On the  $\sigma > 0$  side of the spectrum the C-X bond length difference vs.  $\sigma$  trend levels out because resonance is inhibited for electron withdrawing substituents. For higher  $\sigma$  values, the trend becomes negative meaning that the C-X bond lengths are longer in the planar conformer than in the 90 degree conformer. This results from the fact that when the nitro group is in the planar position, it is withdrawing  $\pi$  electron density from the ring via resonance and therefore is depriving the substituent of that much available  $\pi$  electron density. Thus, when the nitro group moves into the 90 degree position and it can no longer resonate with the ring, this  $\pi$  electron density becomes available once again to the substituent and substituent to ring conjugation is increased; the C-X bond length shortens.

The analogous meta-substituted nitrobenzene relationship is shown in Figure 21. As with the previous meta-substituted relationships, the methoxy substituted nitrobenzene represents a slight anomaly to the overall trend, but again this may be a problem with the geometric optimization caused by the constraining of the methyl

group. The most prominent characteristic of this plot is that it has only a very slight slope, particularly in the  $\sigma > 0$  region. This implies that Structures 5c, 5d and 5e are not major contributors to the electronic structure of m-substituted nitrobenzenes. Another interesting aspect of this relationship is the fact that it becomes increasingly negative in the  $\sigma < 0$  region. Unfortunately, this fact is not readily explainable. It would seem that since  $\text{NO}_2$  is an electron withdrawing group, deviations for strong donating substituents such as  $\text{NH}_2$  would be caused by a small degree of through-resonance via a charge-separated structure such as Structure 4. However, this would lead to the opposite of what is observed in Figure 21. Perhaps the observed deviation is a function of hindrance or some other charge-separation scheme that leads to an increase in  $\pi$  electron density in the ring while the  $\text{NO}_2$  group is in the planar position.

The difference in substituent to ring bond length vs.  $\sigma$  relationships of p-substituted benzoates and benzaldehydes are shown in Figures 29 and 30 respectively. The results are the same as the previously discussed relationships. Because benzaldehydes are much more resonance stabilized than are benzoates, the observed slope for benzaldehydes is notably larger than is the slope for benzoates. Again, the fact that the same relationship is seen between para- and meta-substituted nitrobenzenes is

indicative of a substantial degree of resonance stabilization in p-substituted nitrobenzenes.

#### E. Molecular Orbital Analyses

Another approach that was taken in order to substantiate the results obtained from the analyses of physical parameters was a molecular orbital analysis of the four previously mentioned compounds. The electron populations were determined with the STO-3G basis set using optimized AM1 geometries. This approach is perhaps more direct in that it investigates the electronic structure of these compounds instead of the effects of these electronic configurations upon the molecular structures (bond lengths, torsion angles, etc.). On the other hand, it must be kept in mind that these M.O. calculations are based on theoretical models which in turn are based on observed physical data. Thus, in this way the M.O. approach is more theoretical and therefore less experimentally reproducible than the physical parameter approach. However, the two methods compliment each other nicely, and therefore both have been employed.

##### 1. $p(z)$ Orbital Overlap

The most direct way to investigate the  $\pi$  character of the C-N bond in nitrobenzene is to analyze the overlap of the N and C1 p orbitals. Since the ring was defined as

being planar in the xy plane, the  $p(z)$  orbitals are defined as the  $\pi$  bonding orbitals. Any changes in the  $\pi$  component of the C-N bond will be reflected in the  $p(z)$  orbital overlap. Gaussian 86 yields this information in the form of a density matrix which results from the square of the total wave function and contains terms which are the coefficients of products of the basis set orbitals. These coefficients represent the degree of mixing between the individual atomic orbitals. In this particular case, positive values indicate bonding and negative values indicate anti-bonding. As with the geometric treatment, the important trend to consider is the effect of substituent  $\sigma$  values on the difference in  $p(z)$  overlap between the planar and orthogonal conformers.

This relationship is shown in Figure 31 for p-substituted nitrobenzenes. Clearly, there is a linear relationship between the change in overlap and  $\sigma$  values. The trend is in the direction expected for a compound in which there is a significant amount of  $\pi$  bonding between the ring and the  $\text{NO}_2$  group; more  $p(z)$  orbital overlap occurs with electron donating substituents indicating an increase in the  $\pi$  character of the C-N bond. As with the other trends, a sharp change in slope is observed as the substituents become electron withdrawing. Also, it can be seen that the slope bends back up when the substituent is  $\text{NO}_2$ . Again, this is indicative of competition between the

two identical groups for the available  $\pi$  density in the ring.

The near-zero slopes of the analogous trends for m-substituted nitrobenzenes (Figure 32) and p-substituted benzoates (Figure 33) substantiate the assumption that the correlation observed in Figure 31 for p-substituted nitrobenzenes is indicative of increased C-N  $\pi$  bonding. As expected, p-substituted benzaldehydes exhibit a strong correlation between the change in p(z) orbital overlap and electron donating ability of the substituents, further substantiating this assumption.

## 2. Total Charge on Oxygens

The last parameter that was investigated was the total charge on the NO<sub>2</sub> oxygens. This is of particular interest since this is the same parameter that Lipkowitz analyzed to derive his conclusion that through-resonance does not occur in p-substituted nitrobenzenes. As discussed earlier, the charge on the NO<sub>2</sub> oxygens is related to the contribution from Structure 2e because of all the resonance structures available to p-substituted nitrobenzenes, only 2e results in an increase in the total charge on these oxygens. Whereas Lipkowitz only considered the planar conformer in his analysis, we considered the difference in oxygen charge between the planar and orthogonal conformers as affected by the substituent  $\sigma$  values.

The plot shown in Figure 35 represents the difference in total charge on the NO<sub>2</sub> oxygens vs.  $\sigma$  for p-substituted nitrobenzenes. Contrary to what Lipkowitz reported, there is a definite relationship between these two parameters. The analogous relationship for meta-substituted nitrobenzenes is shown in Figure 36, and it can be seen that the relationship is very slight. The slope of this relationship for p-substituted benzoates (Figure 37) is also very small indicating a small amount of resonance stabilization. Once again, p-substituted benzaldehydes show a significant relationship. Thus, contrary to what Lipkowitz reported, our analysis of the relationship between NO<sub>2</sub> charge density and the electron donating ability of substituents points conclusively to a significant degree of through-resonance stabilization in p-substituted nitrobenzenes.

#### IV. CONCLUSIONS

This study has generated a great deal of qualitative and quantitative data for the electronic substituent effects on the geometries of para and meta-substituted nitrobenzenes. Our approach differed from those of previous studies in that we did not look at one specific compound in determining these effects. Instead we looked at how these effects changed over a spectrum of  $\sigma$  values which represent the electron donating or withdrawing ability of the substituents. In addition, we allowed each

geometry to fully optimize so that variations in experimental geometries would not affect the parameter relationships in which we were interested.

Chief among these parameters was the barrier to rotation of the  $\text{NO}_2$  group about the C-N bond. We have seen that the BTRs for para-substituted nitrobenzenes are definitely and linearly related to the electron donating ability of the substituents. This evidence alone certainly contradicts Lipkowitz's contention that the contribution from Structure 2e is negligible. The very small correlation seen in the BTR vs.  $\sigma$  relationships of para-substituted benzoates and meta-substituted nitrobenzenes supports the idea that para-substituted nitrobenzenes are indeed through-resonance stabilized. Furthermore, because it is shown that very little BTR to  $\sigma$  correlation exists for these two compounds, which are known not to be resonance stabilized, these results lend credibility to the assumption that a linear, non-zero correlation between BTR and  $\sigma$  values indicates a significant contribution from resonance stabilized structures such as 2e.

To substantiate what we have found by looking at the BTR data we also studied in detail several other geometric parameters. The effect of  $\sigma$  values on the C-N bond distance was investigated. It was shown that a relatively high degree of correlation exists between the C-N bond distance and the electronic effects of the substituent for para-substituted nitrobenzenes. In comparison, there was a

much smaller correlation for meta-substituted nitrobenzenes, which are not capable of through-resonance. This again leads to the conclusion that there is a significant degree of conjugation between the nitro group and the ring. The same conclusion was true for the investigation of C2-C3 and C3-C4 bond distances as they related to the  $\sigma$  values of the substituents. We also looked at the electronic effects of substituents on the C-X bond length. Not only did this produce evidence for the presence of through-resonance in para-substituted nitrobenzenes, it also provided the predicted yet necessary evidence that the amount of contribution to the overall structure from Structures 2c-2d and 3b-3c is highly dependent upon the  $\sigma$  value of the substituent. In addition, two electronic parameters were considered. The amount of p(z) orbital overlap between the ring and the NO<sub>2</sub> group was shown to be linearly related to the electron donating ability of the substituents in p-substituted nitrobenzenes and benzaldehydes but not in m-substituted nitrobenzenes and p-substituted benzoates. Finally, by theoretically repeating Lipkowitz's analysis of the total charge density on the NO<sub>2</sub> oxygens over a range of  $\sigma$  values, we obtained results contradictory to the results he obtained from <sup>17</sup>O NMR data.

Finally, the quantitative question remains to be answered. It may very well be possible to extract the relative contributions of Structures 2a-2e solely from

geometric data. If several geometric parameters were studied and the major forces that affect each parameter (for instance, inductive effect, resonance, hindrance, etc.) were broken down into coefficients that described to what degree they affect each parameter, it should be possible to calculate the relative contributions of inductive and resonance electron transfer. This treatment would be very useful as a comparison to some of the other methods of weighting electronic structures that have been reported. Since such data is not available at this time, the only conclusive statement that can be made from the results is that the linearity and consistency of correlation seen in the six relationships that were studied in this investigation do indicate a significant contribution from the through-resonance stabilized Structure (2e) to the overall electronic configuration of para-substituted nitrobenzenes.

For further understanding of the electronic structure of para-substituted nitrobenzenes it would be very useful to investigate many more substituted compounds to fill in the "gaps" in the spectrum of  $\sigma$  values. In addition, it would be interesting to investigate the nature of a benzene compound with a strong electron donating functional group such as aminobenzenes. Finally, it would be helpful to conduct a Mulliken population analysis for each substituted compound to determine the effects of substituent  $\sigma$  values on the electron distribution in the molecules, particularly

the electron density residing within the NO<sub>2</sub> group. From these studies it may be possible to derive a very good quantitative estimation of the relative contribution of Structure 2e to the overall electronic structure of para-substituted nitrobenzenes.

### Acknowledgments

I would like to thank the Trident Scholar program at the United States Naval Academy for sponsoring this project. I would also like to acknowledge Dr. D. Dudis of Wright-Patterson Air Force Base for his assistance with this work. Lastly, I would like to thank my adviser, Dr. Wayne Pearson, for the many long hours he contributed to this project. Without his help and guidance, this project could never have been realized.

Table 1. Barrier to Rotation (kJ/mol) for para-substituted nitrobenzenes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OH	NH <sub>2</sub>
Sigma	0.78	0.66	0.23	0.18	0.15	0.00	0.00	-0.37	-0.37	-0.66
BARRIER	13.62	13.92	14.31	14.63	15.43	14.53	15.61	16.40	16.80	18.95

Table 2. Bond Lengths (Angstroms) for para-substituted nitrobenzenes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OH	NH <sub>2</sub>
Sigma	0.78	0.66	0.23	0.18	0.15	0.00	0.00	-0.37	-0.37	-0.66
C1-N(planar)	1.4921	1.4892	1.4877	1.4883	1.4854	1.4865	1.4848	1.4821	1.4823	1.4767
C1-N(ortho)	1.4908	1.4972	1.4961	1.4964	1.4959	1.4955	1.4947	1.4931	1.4925	1.4907
delta C1-N	0.0067	0.0088	0.0084	0.0081	0.0102	0.0090	0.0099	0.0110	0.0118	0.0140
C2-C3(planar)	1.3927	1.3923	1.3926	1.3927	1.3914	1.3921	1.3913	1.3884	1.3883	1.3830
C2-C3(ortho)	1.3932	1.3932	1.3928	1.3947	1.3929	1.3943	1.3927	1.3902	1.3901	1.3835
delta C2-C3	0.0005	0.0009	0.0012	0.0010	0.0015	0.0012	0.0014	0.0018	0.0018	0.0025
C3-C4(planar)	1.4035	1.4022	1.3988	1.3956	1.3986	1.3954	1.3998	1.4074	1.4062	1.4225
C3-C4(ortho)	1.4039	1.4019	1.3984	1.3953	1.3978	1.3948	1.3990	1.4063	1.4051	1.4208
delta C3-C4	-0.0002	-0.0003	-0.0004	-0.0003	-0.0008	-0.0006	-0.0008	-0.0011	-0.0011	-0.0017
C4-X(planar)	1.4922	1.4724	1.8791	2.0199	1.5063	1.1008	1.0905	1.5758	1.5696	1.5696
C4-X(ortho)	1.4913	1.4722	1.8792	2.0199	1.5064	1.1008	1.0920	1.5778	1.5714	1.5719
delta C4-X	-0.0009	-0.0002	0.0001	0.0000	-0.0001	0.0000	0.0015	0.0020	0.0018	0.0023

Table 3. Coefficients for C1 p(s)-Np(s) orbital overlap for para-substituted nitrobenzenes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OH	NH <sub>2</sub>
Sigma	0.78	0.66	0.23	0.18	0.15	0.00	0.00	-0.37	-0.37	-0.66
Planar	0.1032	0.0908	0.1008	0.0999	0.1053	0.1056	0.1022	0.1104	0.1105	0.1230
Orthogonal	0.0026	0.0035	0.0031	0.0034	0.0021	0.0028	0.0026	0.0007	0.0008	-0.0001

Table 4. Total charge density on oxygen in para-substituted nitrobenzenes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OH	NH <sub>2</sub>
Sigma	0.78	0.66	0.23	0.18	0.15	0.00	0.00	-0.37	-0.37	-0.66
Planar	-0.3516	-0.3426	-0.3463	-0.3469	-0.3516	-0.3526	-0.3517	-0.3508	-0.3502	-0.3453
Orthogonal	-0.3377	-0.3294	-0.3326	-0.3327	-0.3355	-0.3342	-0.3377	-0.3368	-0.3383	-0.3456

Table 5. Barrier to Rotation (kJ/mol) for meta-substituted nitrobenzenes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	OH	NH <sub>2</sub>
sigma	0.71	0.56	0.39	0.35	0.25	0	0.15	0.12	-0.12	-0.16
BARRIER	13.10	14.52	14.59	14.72	14.95	14.53	16.29	15.52	16.12	13.10

Table 6. Bond Lengths (Angstroms) for meta-substituted nitrobenzenes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	OH	NH <sub>2</sub>
Sigma	0.71	0.56	0.39	0.35	0.25	0	0.15	0.12	-0.12	-0.16
Cl-N(phenyl)	1.4099	1.4091	1.4080	1.4076	1.4064	1.4053	1.4052	1.4053	1.4059	1.4063
Cl-N(ortho)	1.4081	1.4074	1.4066	1.4063	1.4055	1.4045	1.4049	1.4077	1.4071	1.4083
delta Cl-N	0.0082	0.0083	0.0086	0.0087	0.0081	0.0090	0.0087	0.0084	0.0082	0.0080
Cl-C(phenyl)	1.4025	1.4121	1.3946	1.3923	1.3943	1.3931	1.3934	1.3928	1.3993	1.4167
Cl-C(ortho)	1.4040	1.4136	1.3929	1.3943	1.3956	1.3943	1.3948	1.3968	1.4009	1.4181
delta Cl-C	0.0015	0.0015	0.0013	0.0010	0.0013	0.0012	0.0014	0.0010	0.0016	0.0014
C3-C4(phenyl)	1.4053	1.3999	1.3968	1.3928	1.3962	1.3954	1.3975	1.4142	1.4074	1.4196
C3-C4(ortho)	1.4040	1.3991	1.3944	1.3923	1.3928	1.3948	1.3969	1.4137	1.4071	1.4200
delta C3-C4	-0.0012	-0.0008	-0.0004	-0.0006	-0.0004	-0.0006	-0.0006	-0.0005	-0.0003	0.0004
C4-X(phenyl)	1.4910	1.4350	1.4715	2.0195	1.6832	1.1007	1.6954	1.3025	1.3754	1.3008
C4-X(ortho)	1.4911	1.4352	1.4715	2.0196	1.6847	1.1007	1.6954	1.3018	1.3746	1.3798
delta C4-X	0.0001	0.0002	0.0000	0.0001	-0.0005	0.0000	0.0000	-0.0007	-0.0008	-0.0010

Table 7. Coefficients for C1p(x)-N1p(x) overlap for meta-substituted nitrobenzenes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	OH	NH <sub>2</sub>
Sigma	0.71	0.56	0.39	0.35	0.25	0	0.15	0.12	-0.12	-0.16
Phenyl	0.0927	0.0902	0.1003	0.1008	0.1012	0.1056	0.1023	0.1018	0.1008	0.1010
Orthogonal	0.0009	0.0017	0.0022	0.0021	0.0020	0.0020	0.0021	0.0020	0.0020	0.0017

Table 8. Total charge density on oxygen in meta-substituted nitrobenzenes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	OH	NH <sub>2</sub>
Sigma	0.71	0.56	0.39	0.35	0.25	0	0.15	0.12	-0.12	-0.16
Phenyl	-0.3027	-0.3412	-0.3451	-0.3439	-0.3396	-0.3326	-0.3267	-0.3256	-0.3208	-0.3253
Orthogonal	-0.3222	-0.3206	-0.3221	-0.3227	-0.3241	-0.3242	-0.3234	-0.3235	-0.3251	-0.3265

Table 9. Barrier to Rotation (kJ/mol) for para-substituted benzoates

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	OH	NH <sub>2</sub>
sigma	6.78	6.66	6.23	6.18	6.15	6.00	6.00	-6.27	-6.37	-6.66
BARRIER	6.24	6.64	7.695	6.81596	7.646	8.13637	6.93	8.7787	8.45	9.82

Table 10. Bond Lengths (Angstroms) for para-substituted benzoates

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	OH	NH <sub>2</sub>
Sigma	6.78	6.66	6.23	6.18	6.15	6.00	6.00	-6.27	-6.37	-6.66
C1-C7 (plane)	1.5283	1.5251	1.5236	1.5238	1.5234	1.5210	1.5225	1.5211	1.5208	1.5177
C1-C7 (ortho)	1.5289	1.5260	1.5248	1.5252	1.5246	1.5221	1.5217	1.5233	1.5229	1.5285
delta C1-C7	0.0006	0.0009	0.0012	0.0014	0.0016	0.0011	0.0022	0.0022	0.0021	0.0028
C2-C3 (plane)	1.3912	1.3928	1.3947	1.3952	1.3954	1.3955	1.3944	1.3937	1.3949	1.3919
C2-C3 (ortho)	1.3899	1.3919	1.3938	1.3939	1.3946	1.3948	1.3928	1.3940	1.3943	1.3916
delta C2-C3	-0.0013	-0.0009	-0.0009	-0.0013	-0.0008	-0.0007	-0.0116	0.0003	-0.0006	-0.0003
C3-C4 (plane)	1.4072	1.4033	1.3971	1.3971	1.3954	1.3951	1.3969	1.4023	1.4009	1.4146
C3-C4 (ortho)	1.4073	1.4033	1.3970	1.3951	1.3953	1.3948	1.4022	1.4019	1.4005	1.4139
delta C3-C4	0.0001	0.0000	-0.0001	0.0000	-0.0001	-0.0003	0.0033	-0.0004	-0.0004	-0.0007
C4-X (plane)	1.4763	1.4198	1.8032	2.0264	1.6958	1.6981	1.7059	1.3953	1.3858	1.3885
C4-X (ortho)	1.4746	1.4193	1.8024	2.0263	1.6958	1.6980	1.7059	1.3959	1.3864	1.3903
delta C4-X	-0.0016	-0.0005	-0.0008	-0.0002	0.0000	-0.0001	0.0000	0.0006	0.0006	0.0008

Table 11. Coefficients for C1 p(z)-N p(z) orbital overlap for para-substituted benzoates

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	OH	NH <sub>2</sub>
Sigma	6.78	6.66	6.23	6.18	6.15	6.00	6.00	-6.27	-6.37	-6.66
Plane	0.0489	0.0474	0.0453	0.0465	0.0456	0.0456	0.0456	0.0448	0.0447	0.0451
Orthogonal	-0.0095	-0.0138	-0.0153	-0.0147	-0.0176	-0.0179	-0.0175	-0.0203	-0.0209	-0.0234

Table 12. Total charge density on oxygen in para-substituted benzoates

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	OH	NH <sub>2</sub>
Sigma	6.78	6.66	6.23	6.18	6.15	6.00	6.00	-6.27	-6.37	-6.66
Plane	-0.5729	-0.5813	-0.5856	-0.5851	-0.5896	-0.5933	-0.5984	-0.5929	-0.5942	-0.5997
Orthogonal	-0.5678	-0.5754	-0.5793	-0.5788	-0.5831	-0.5871	-0.5798	-0.5851	-0.5868	-0.5917

Table 13. Barrier to Rotation (kJ/mol) for para-substituted benzaldehydes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OH	NH <sub>2</sub>
Sigma	0.78	0.66	0.23	0.18	0.15	0.00	0.00	-0.27	-0.37	-0.66
BARRIER	8.43	9.79	10.41	10.13	11.97	11.18	12.65	14.13	13.66	15.97

Table 14. Bond Lengths (Angstroms) for para-substituted benzaldehydes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OH	NH <sub>2</sub>
Sigma	0.78	0.66	0.23	0.18	0.15	0.00	0.00	-0.27	-0.37	-0.66
C1-C7 (plane)	1.4774	1.4744	1.4731	1.4735	1.4713	1.4714	1.4709	1.4687	1.4687	1.4643
C1-C7 (ortho)	1.483	1.4803	1.4793	1.4795	1.4781	1.4784	1.4785	1.4776	1.4776	1.4732
delta C1-C7	0.0046	0.0059	0.0052	0.0060	0.0068	0.0070	0.0076	0.0089	0.0089	0.0110
C2-C3 (plane)	1.3927	1.3926	1.3932	1.3941	1.3924	1.3935	1.3923	1.3899	1.3897	1.3859
C2-C3 (ortho)	1.3937	1.3931	1.3937	1.3945	1.3923	1.3943	1.3923	1.3913	1.3911	1.3870
delta C2-C3	0.0000	0.0005	0.0005	0.0004	0.0009	0.0008	0.0010	0.0014	0.0014	0.0020
C3-C4 (plane)	1.4039	1.4024	1.3986	1.3957	1.3980	1.3953	1.3991	1.4064	1.4053	1.4209
C3-C4 (ortho)	1.4041	1.4020	1.3981	1.3955	1.3974	1.3950	1.3983	1.4053	1.4043	1.4190
delta C3-C4	0.0002	-0.0004	-0.0003	-0.0002	-0.0006	-0.0005	-0.0008	-0.0013	-0.0011	-0.0019
C4-X (plane)	1.4095	1.4230	1.4724	2.0209	1.4044	1.1000	1.4934	1.3897	1.3727	1.3731
C4-X (ortho)	1.408	1.4219	1.4723	2.0204	1.4040	1.1000	1.4947	1.3886	1.3746	1.3739
delta C4-X	-0.0015	-0.0014	-0.0001	-0.0005	0.0016	0.0009	0.0013	-0.0011	0.0019	0.0028

Table 15. Coefficients for C1p(O)-C7p(O) orbital overlap for para-substituted benzaldehydes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OH	NH <sub>2</sub>
Sigma	0.78	0.66	0.23	0.18	0.15	0.00	0.00	-0.27	-0.37	-0.66
Plane	0.0999	0.0956	0.0960	0.0972	0.1039	0.1031	0.1016	0.1064	0.1089	0.1209
Orthogonal	-0.0107	-0.0120	-0.0125	-0.0117	-0.0149	-0.0139	-0.0191	-0.0177	-0.0183	-0.0187

Table 16. Total charge density on oxygen in para-substituted benzaldehydes

Substituent	NO <sub>2</sub>	CN	Br	I	SH	H	SC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OH	NH <sub>2</sub>
Sigma	0.78	0.66	0.23	0.18	0.15	0.00	0.00	-0.27	-0.37	-0.66
Plane	-0.2903	-0.3006	-0.3133	-0.3126	-0.3197	-0.3203	-0.3285	-0.3202	-0.3203	-0.3278
Orthogonal	-0.3204	-0.3300	-0.3375	-0.3374	-0.3529	-0.3545	-0.3599	-0.3570	-0.3577	-0.3595

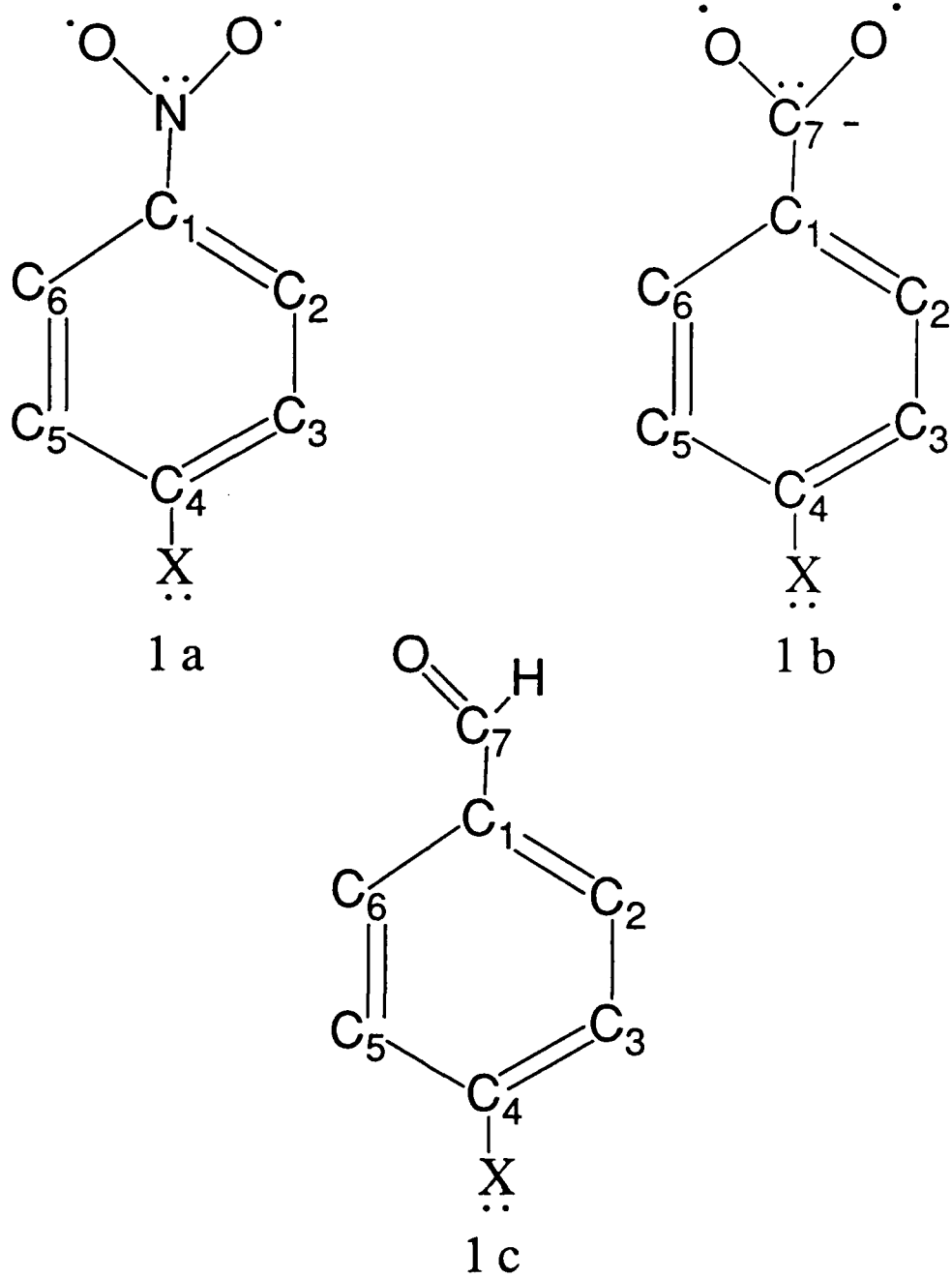


Figure 1. Atom positions for substituted nitrobenzene, benzoate and benzaldehyde.

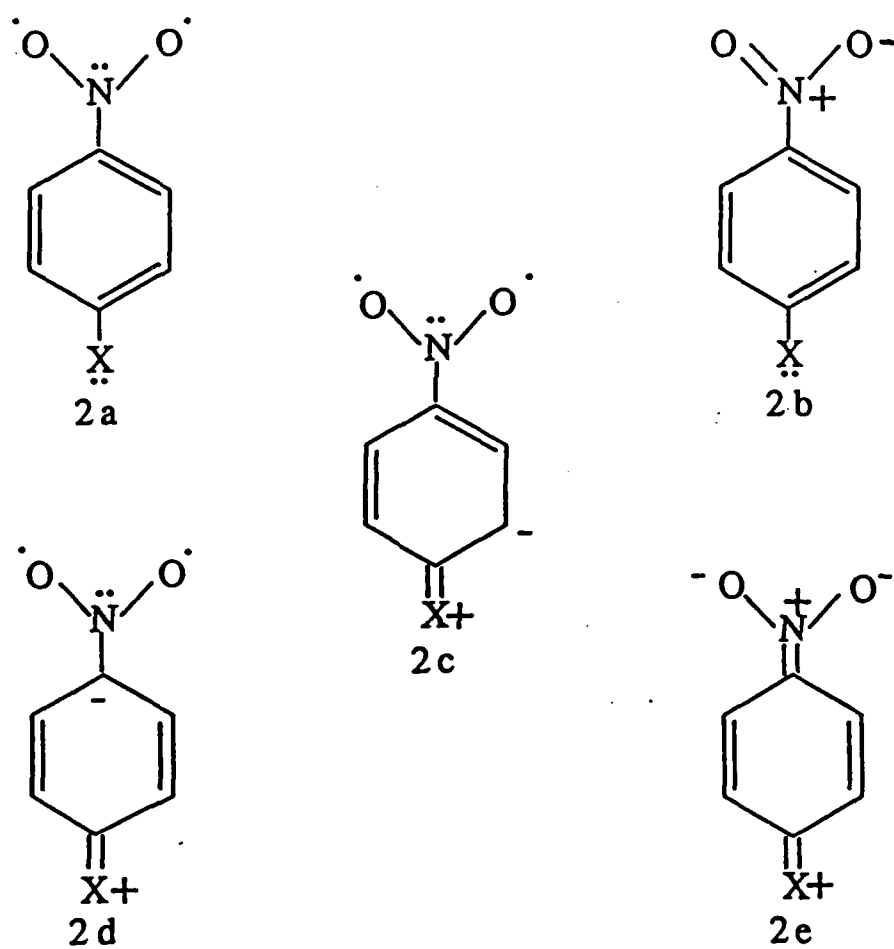


Figure 2. Resonance Structures for substituted nitrobenzenes with electron donating groups

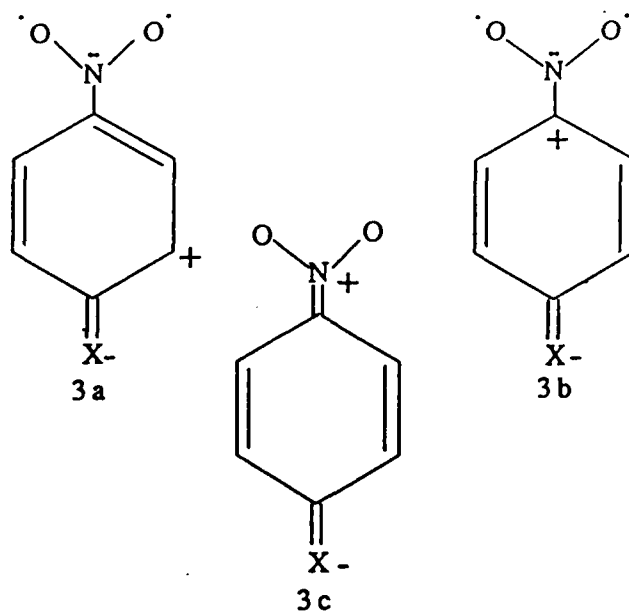


Figure 3. Resonance structures for substituted nitrobenzenes with electron withdrawing groups

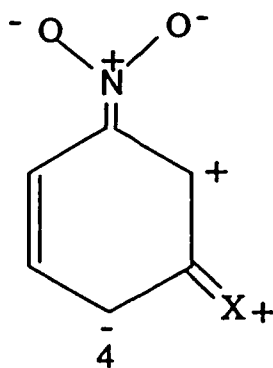


Figure 4. Highly charge separated resonance structure for meta through resonance

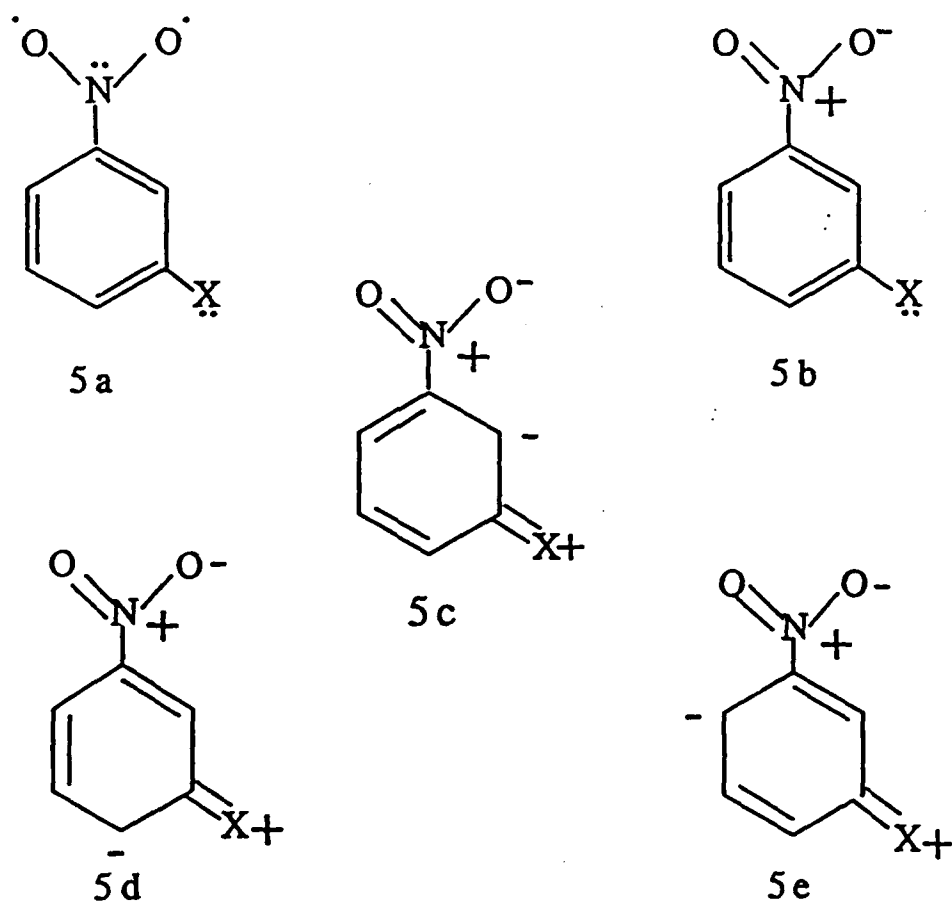


Figure 5. Resonance structures for meta substituted nitrobenzenes with electron donating groups

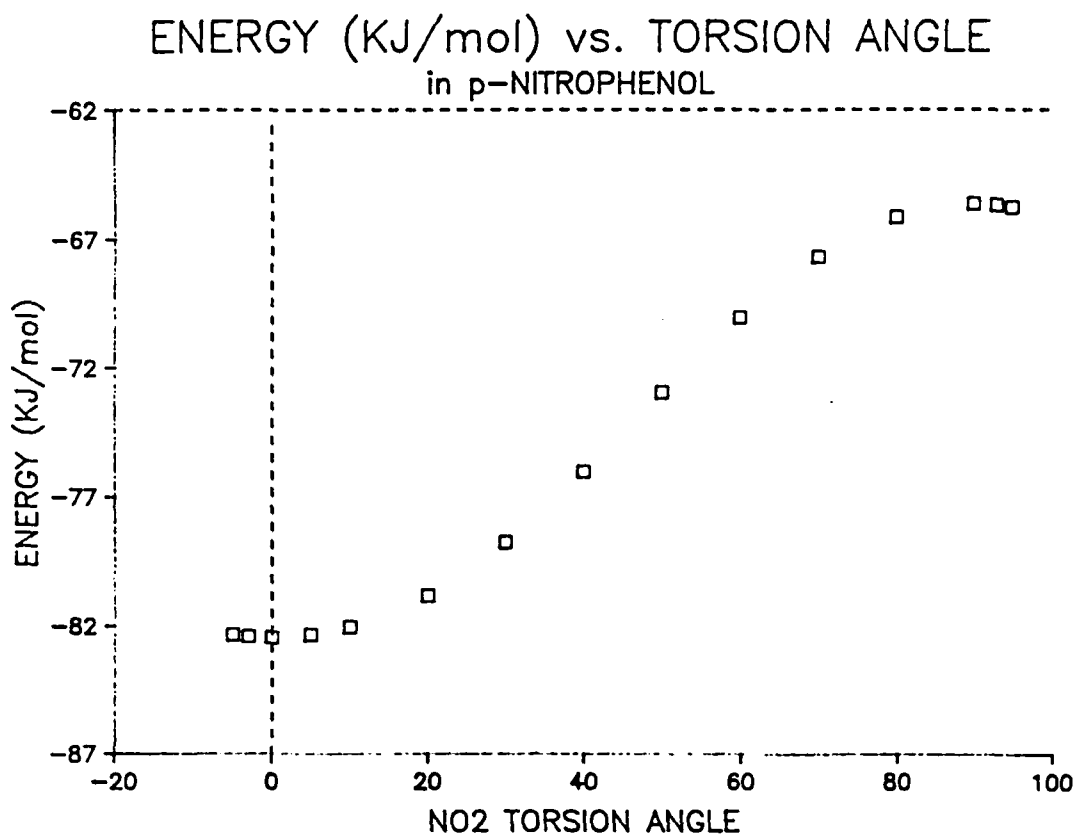


Figure 6. Rotational analysis of p-nitrophenol confirming that the planar conformer is more stable than the orthogonal conformer.

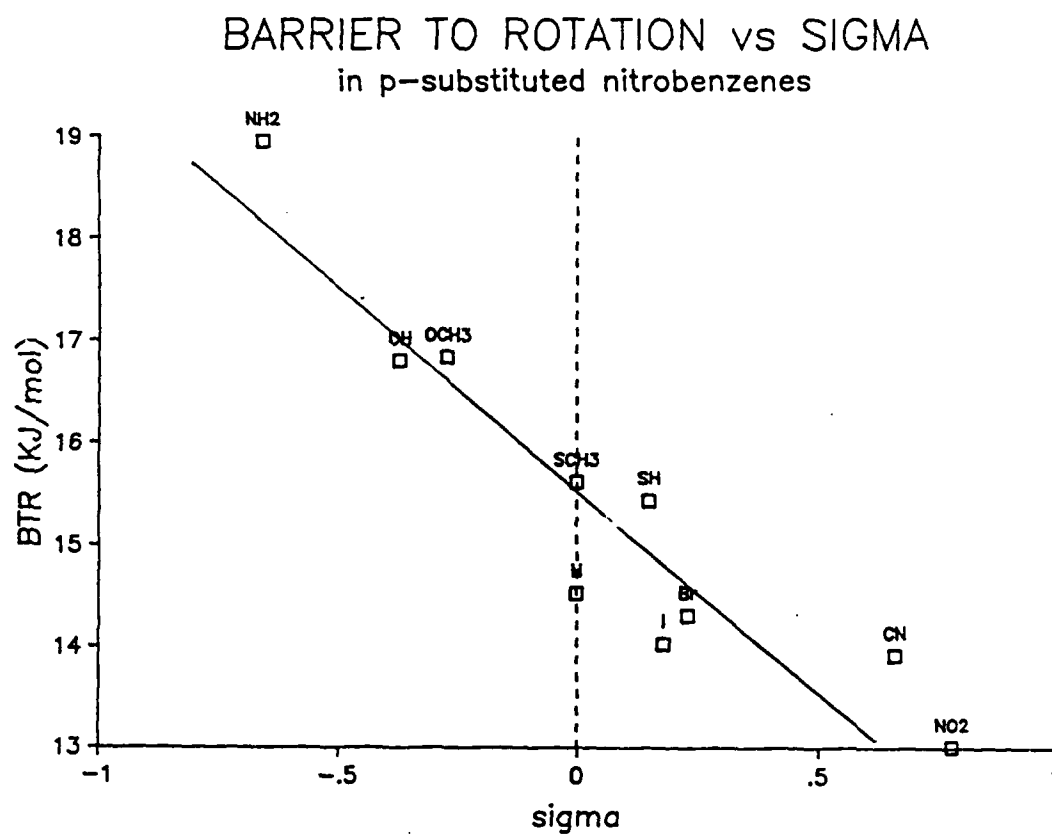


Figure 7a. The effect of  $\sigma$  values on the BTR of p-substituted nitrobenzenes. Slope =  $-3.74 \text{ kJ/mol}\cdot\sigma$ .

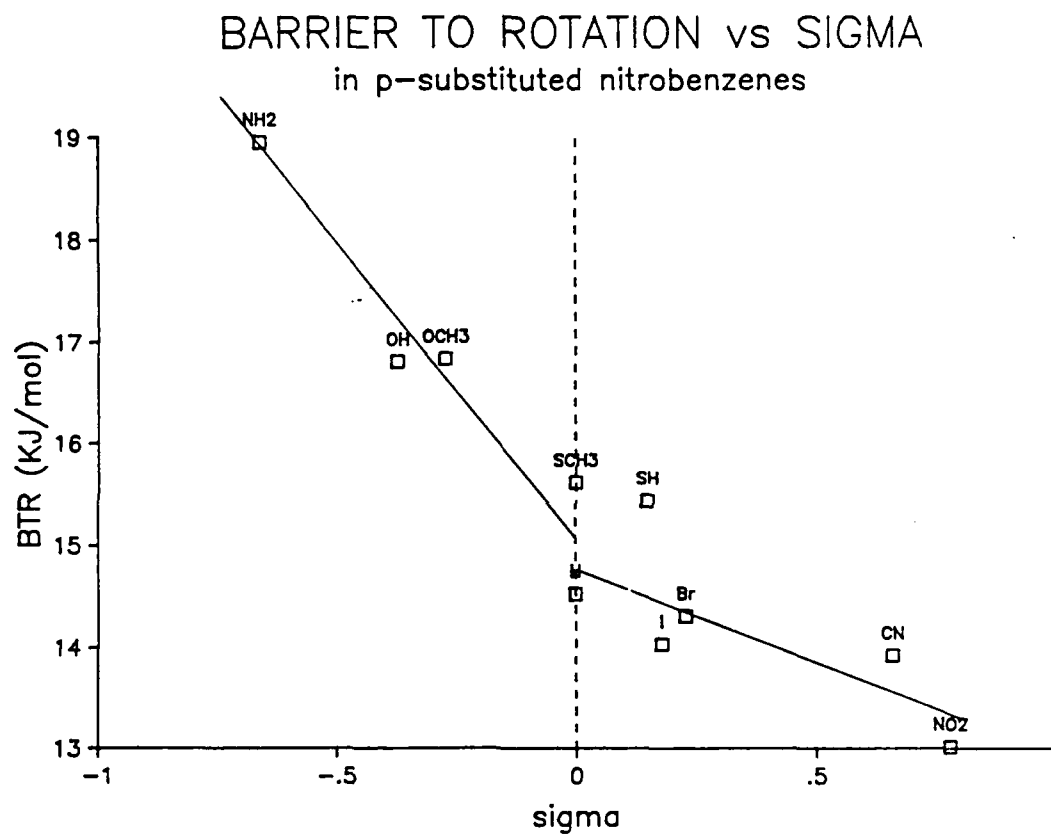


Figure 7b. Plot indicating the sharp decrease in the BTR vs.  $\sigma$  relationship as  $\sigma$  values become positive. Slope of 7b(-) =  $-5.87 \pm 1.57 \text{ kJ/mol} \cdot \sigma$ ; slope of 7b(+) =  $-2.31 \text{ kJ/mol} \cdot \sigma$ .

BARRIER TO ROTATION vs SIGMA  
in p-substituted benzoates

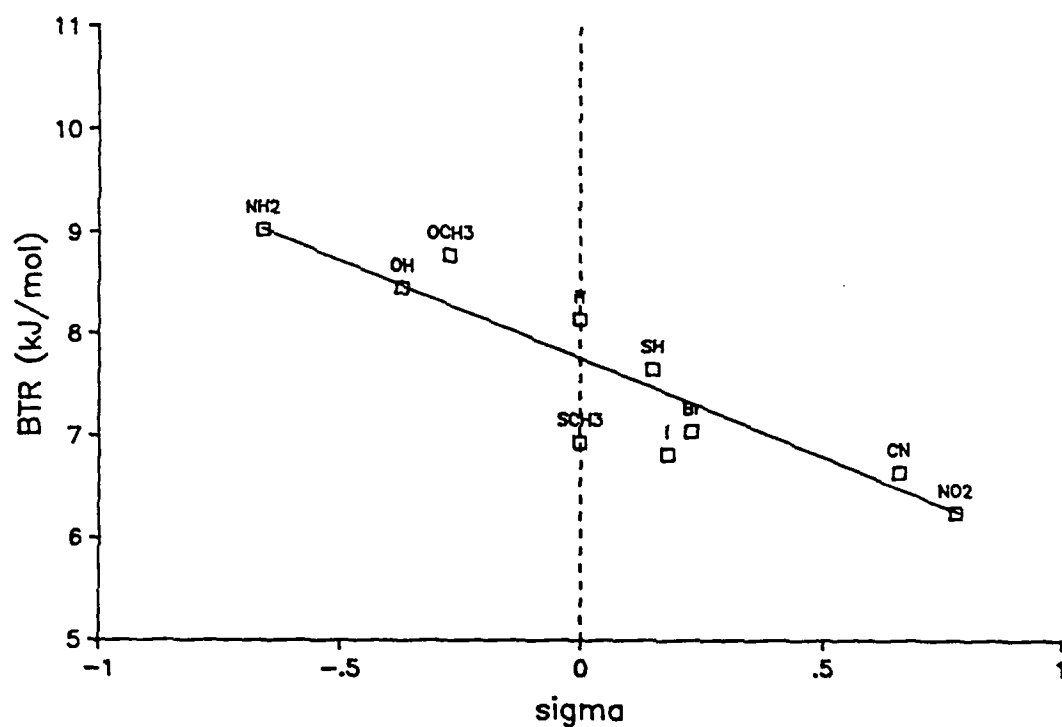


Figure 8. The effect of  $\sigma$  values on the BTR of p-substituted benzoates. Slope =  $-2.004 \text{ kJ/mol} \cdot \sigma$ .

BTR vs. SIGMA VALUES  
in meta-substituted nitrobenzenes

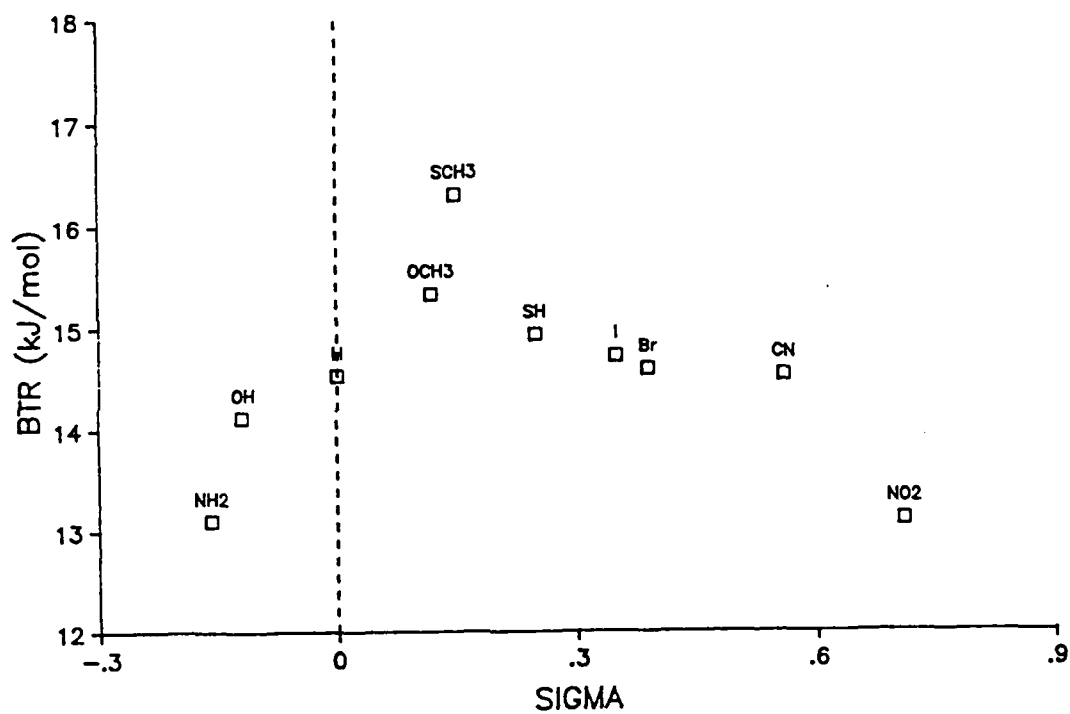


Figure 9. The effect of  $\sigma$  values on the BTR of *m*-substituted nitrobenzenes.

# BARRIER TO ROTATION vs SIGMA in p-substituted benzaldehydes

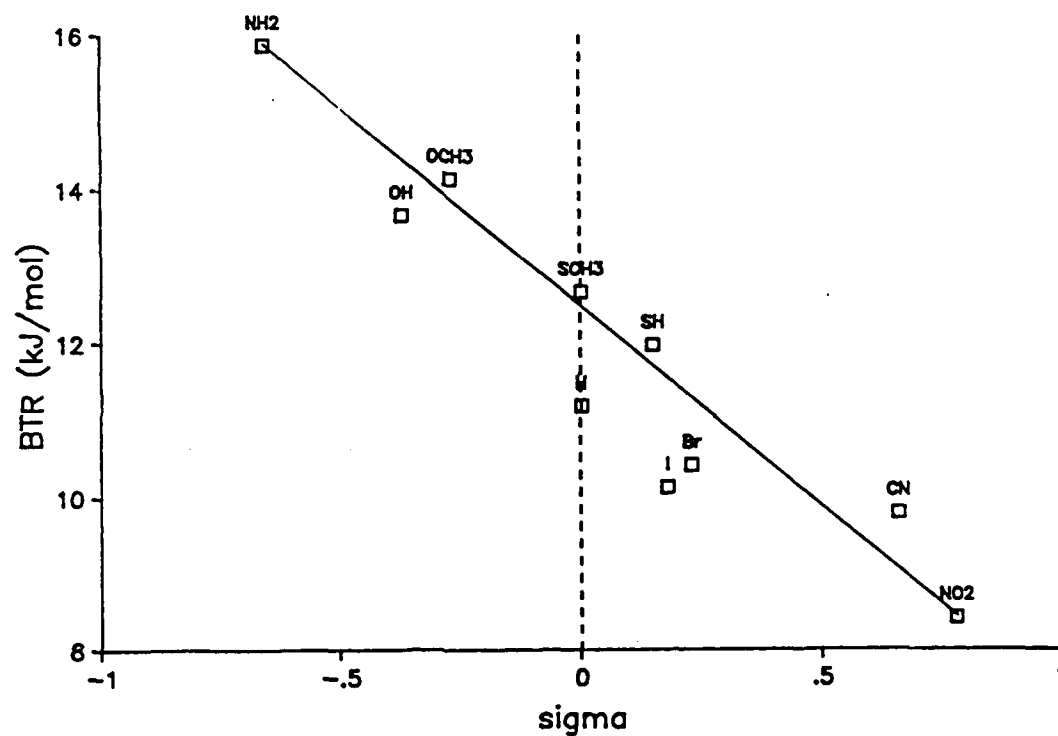


Figure 10. The effect of  $\sigma$  values on the BTR of p-substituted benzaldehydes. Slope =  $-4.906 \text{ kJ/mol} \cdot \sigma$ .

# C-N BOND DISTANCE vs SIGMA in p-substituted nitrobenzenes

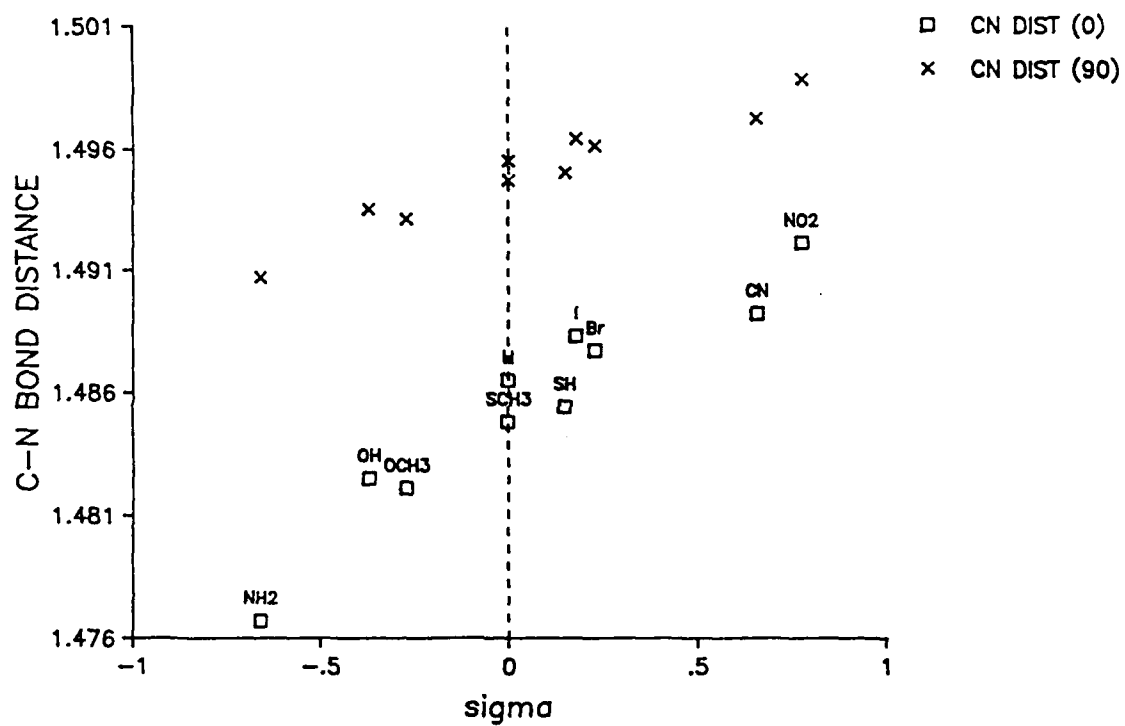


Figure 11. The effect of  $\sigma$  values on the C-N bond distances of the 0 and 90 degree conformers of p-substituted nitrobenzenes.

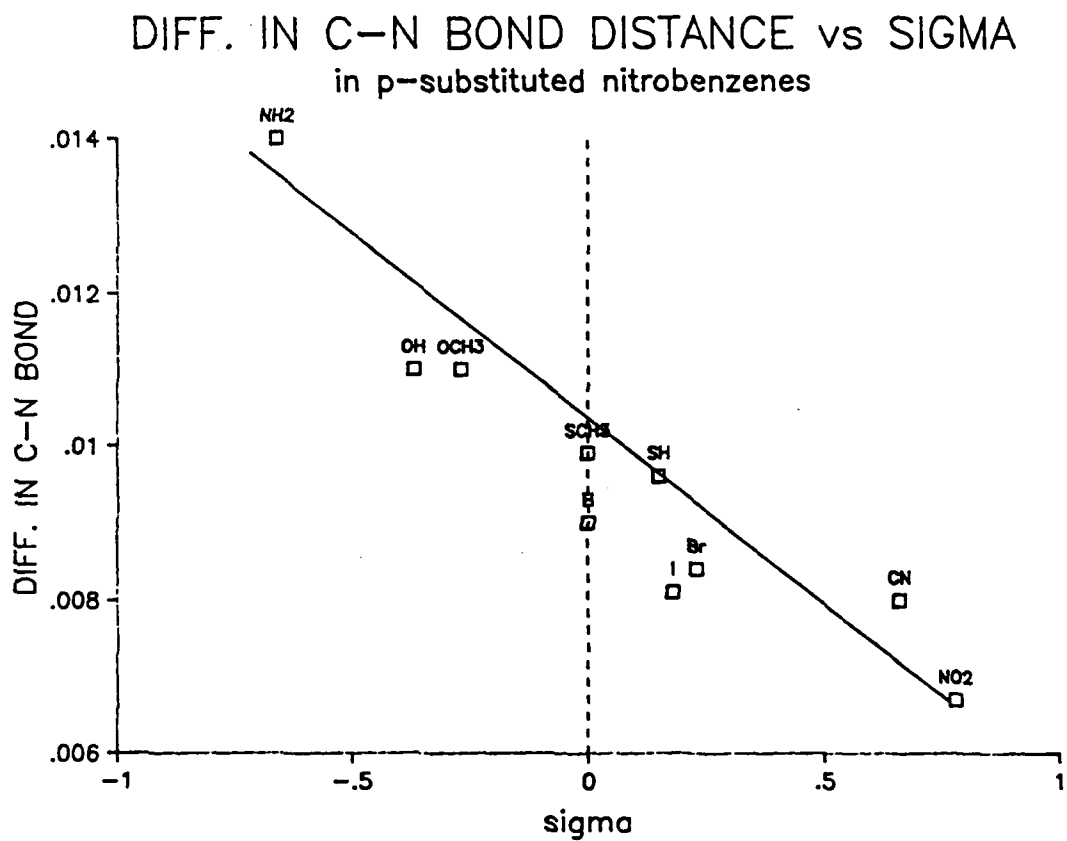


Figure 12. The effect of  $\sigma$  values on the change in C-N bond distances of p-substituted nitrobenzenes as the NO<sub>2</sub> group is rotated 90 degrees out of the plane of the ring. Slope =  $-4.37 \times 10^{-3} \text{ \AA/mol} \cdot \sigma$ .

# C-N BOND DISTANCE vs SIGMA in meta-substituted nitrobenzenes

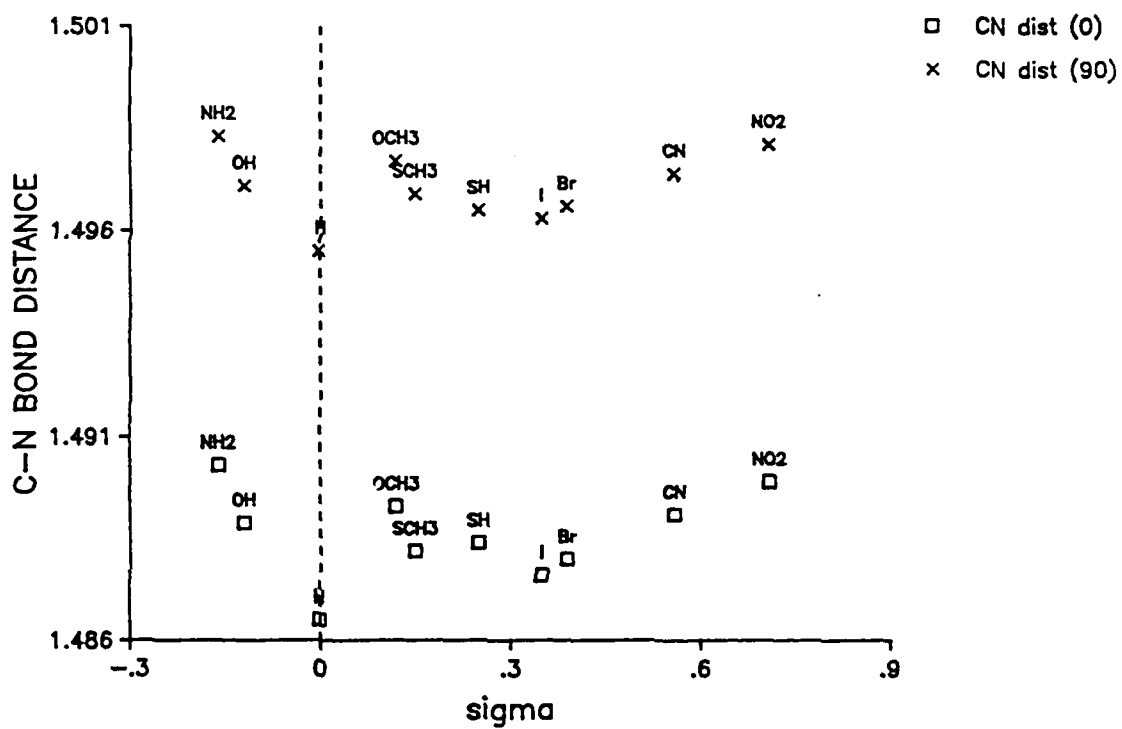


Figure 13. The effect of  $\sigma$  values on the C-N bond distances of the 0 and 90 degree conformers of m-substituted nitrobenzenes.

DIFF. IN CN BOND DISTANCE vs SIGMA  
in meta-substituted nitrobenzenes

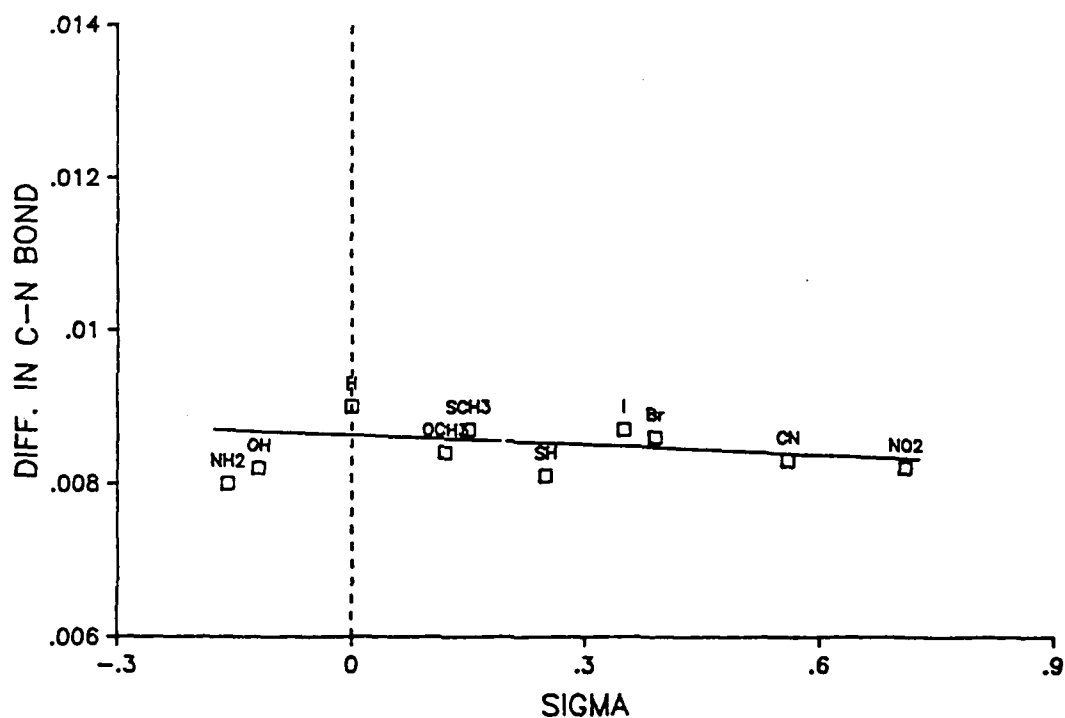


Figure 14. The effect of  $\sigma$  values on the change in C-N bond distances of m-substituted nitrobenzenes as the NO<sub>2</sub> group is rotated 90 degrees out of the plane of the ring. Slope =  $-8.17 \times 10^{-4}$  Å/mol.  $\sigma$ .

# C1-C7 BOND DISTANCE vs SIGMA in p-substituted benzoates

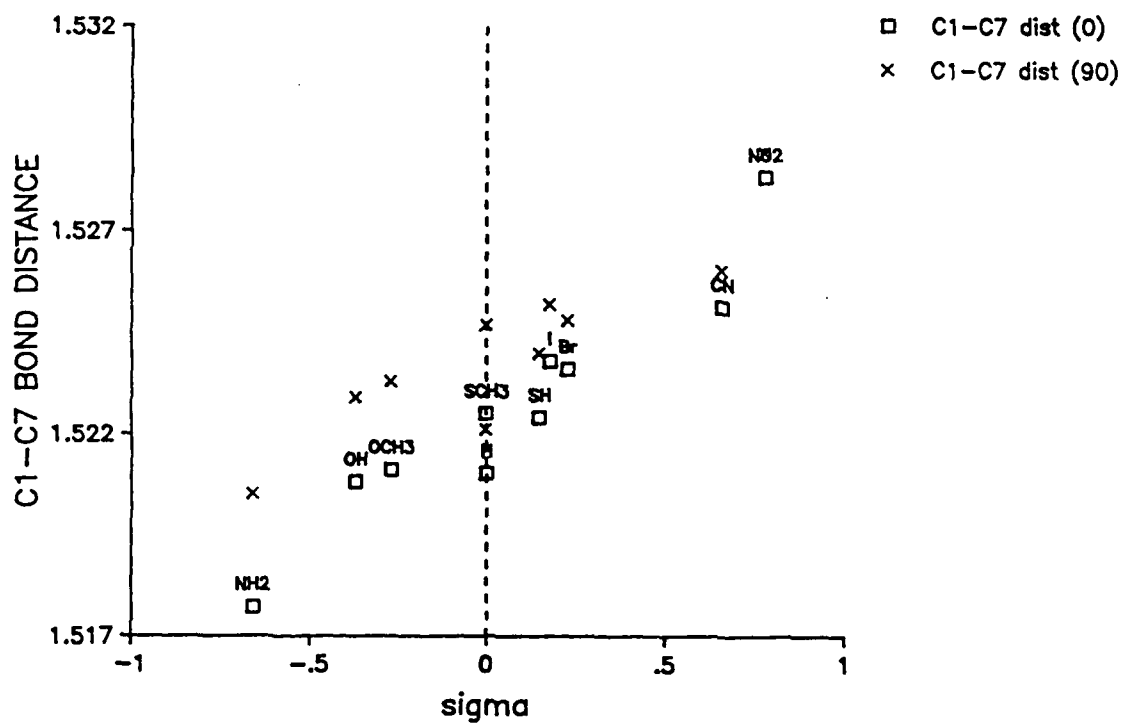


Figure 15. The effect of  $\sigma$  values on the C1-C7 bond distances of the 0 and 90 degree conformers of p-substituted benzoates.

# DIFF. IN C1-C7 BOND DISTANCE vs SIGMA in p-substituted benzoates

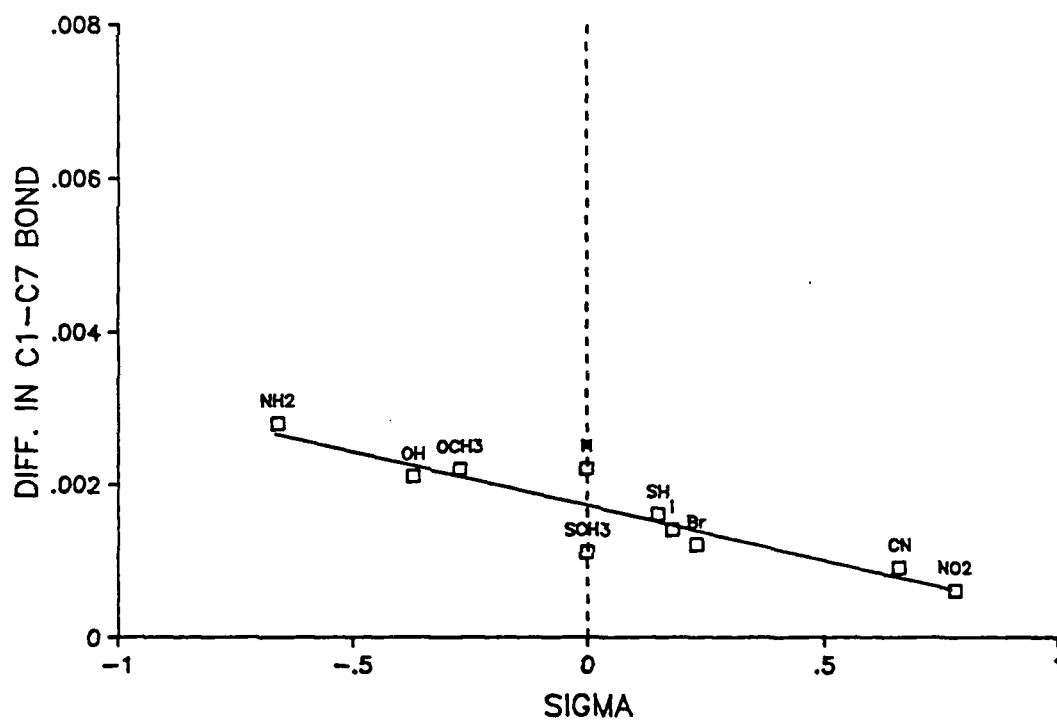


Figure 16. The effect of  $\sigma$  values on the change in C1-C7 bond distances of p-substituted benzoates as the COO' group is rotated 90 degrees out of the plane of the ring. Slope =  $-1.439 \times 10^{-2}$  Å/mol. $\sigma$ .

# C1-C7 BOND DISTANCE vs SIGMA in p-substituted benzaldehydes

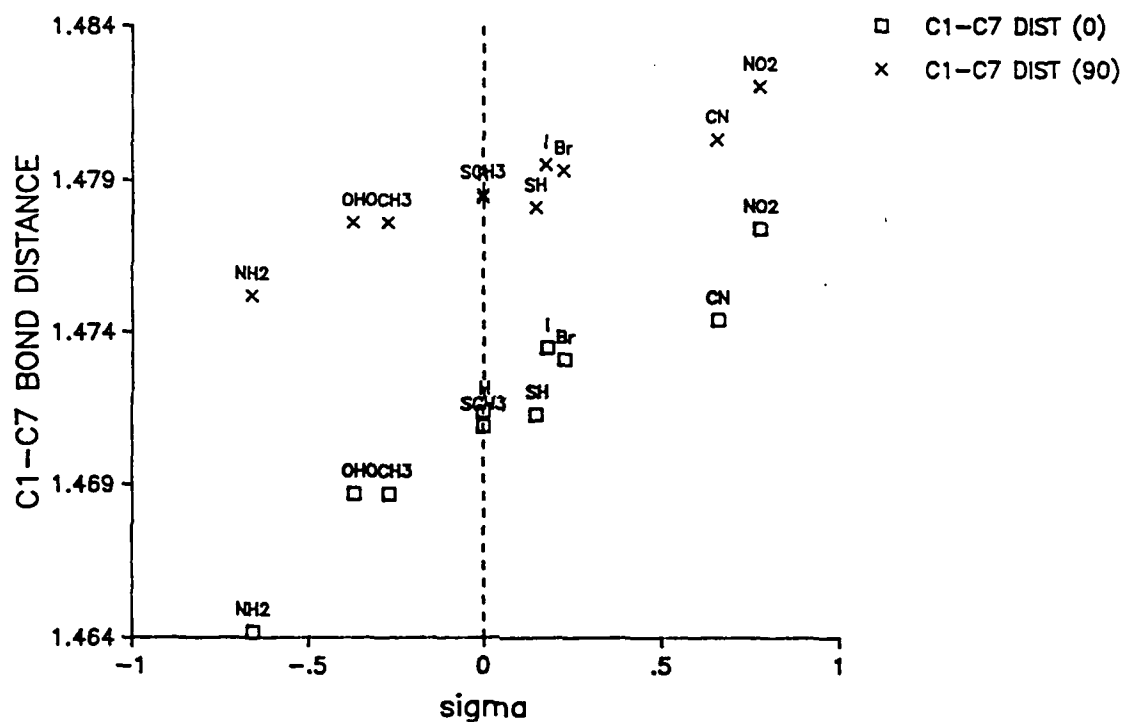


Figure 17. The effect of  $\sigma$  values on the C1-C7 bond distances of the 0 and 90 degree conformers of p-substituted benzaldehydes.

# DIFF. IN C1-C7 BOND DISTANCE vs SIGMA in p-substituted benzaldehydes

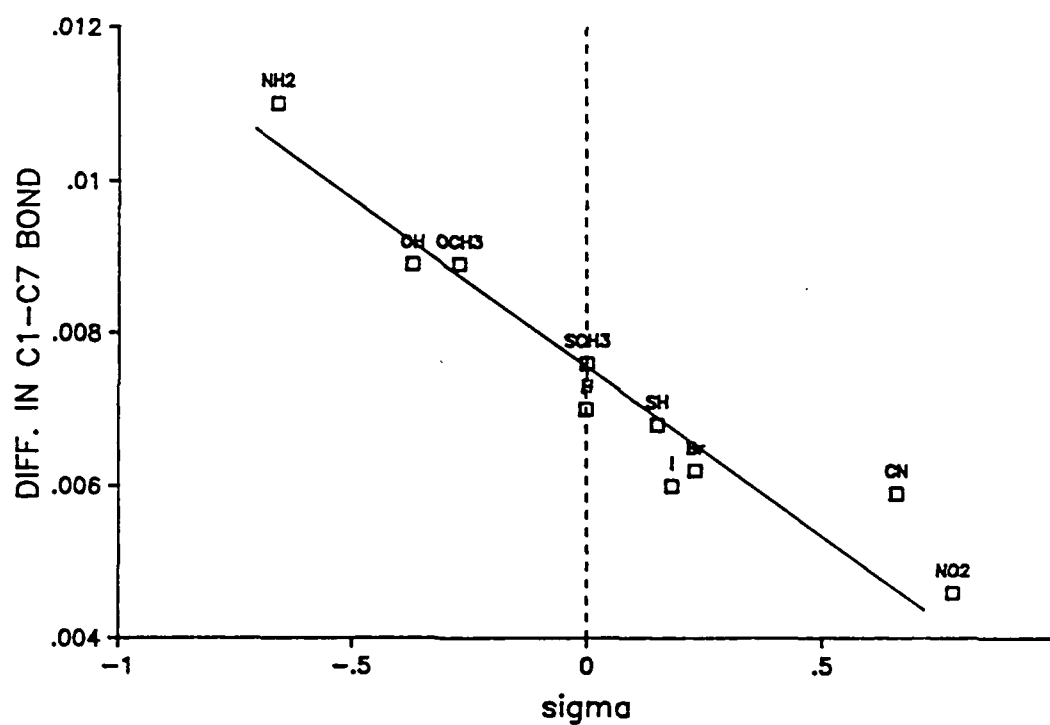


Figure 18. The effect of  $\sigma$  values on the change in C1-C7 bond distances of p-substituted benzaldehydes as the CHO group is rotated 90 degrees out of the plane of the ring. Slope =  $-4.033 \times 10^{-3} \text{ \AA/mol} \cdot \sigma$ .

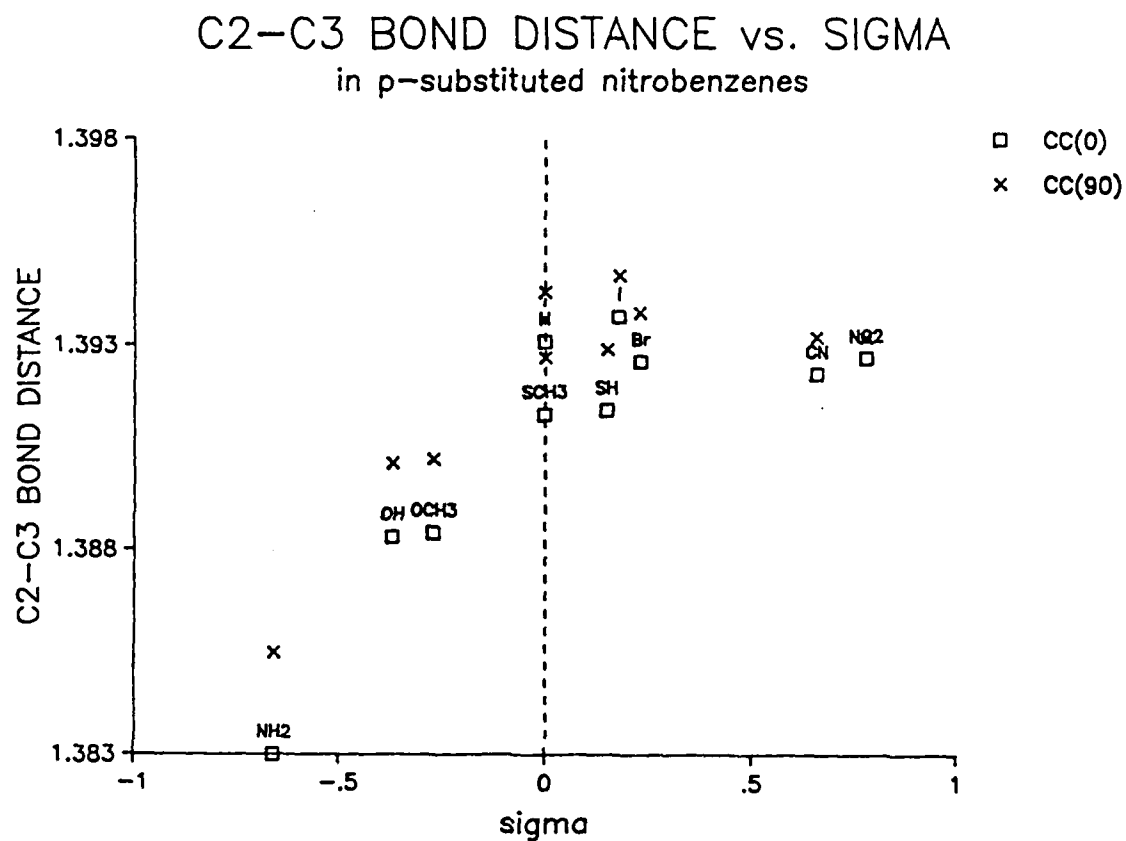


Figure 19. The effect of  $\sigma$  values on the C2-C3 bond distances of the 0 and 90 degree conformers of p-substituted nitrobenzenes.

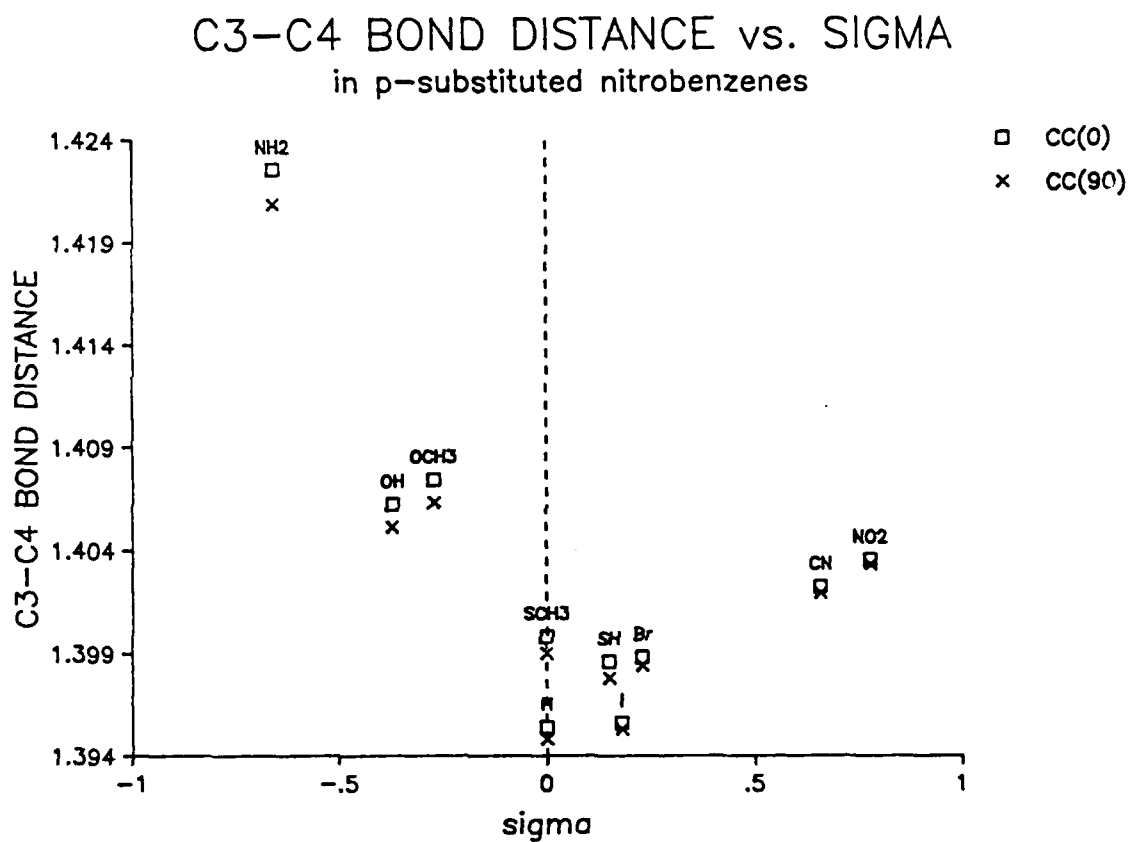


Figure 20. The effect of  $\sigma$  values on the C3-C4 bond distances of the 0 and 90 degree conformers of p-substituted nitrobenzenes.

# DIFF.IN C2-C3 AND C3-C4 BOND DISTANCES in p-substituted nitrobenzenes

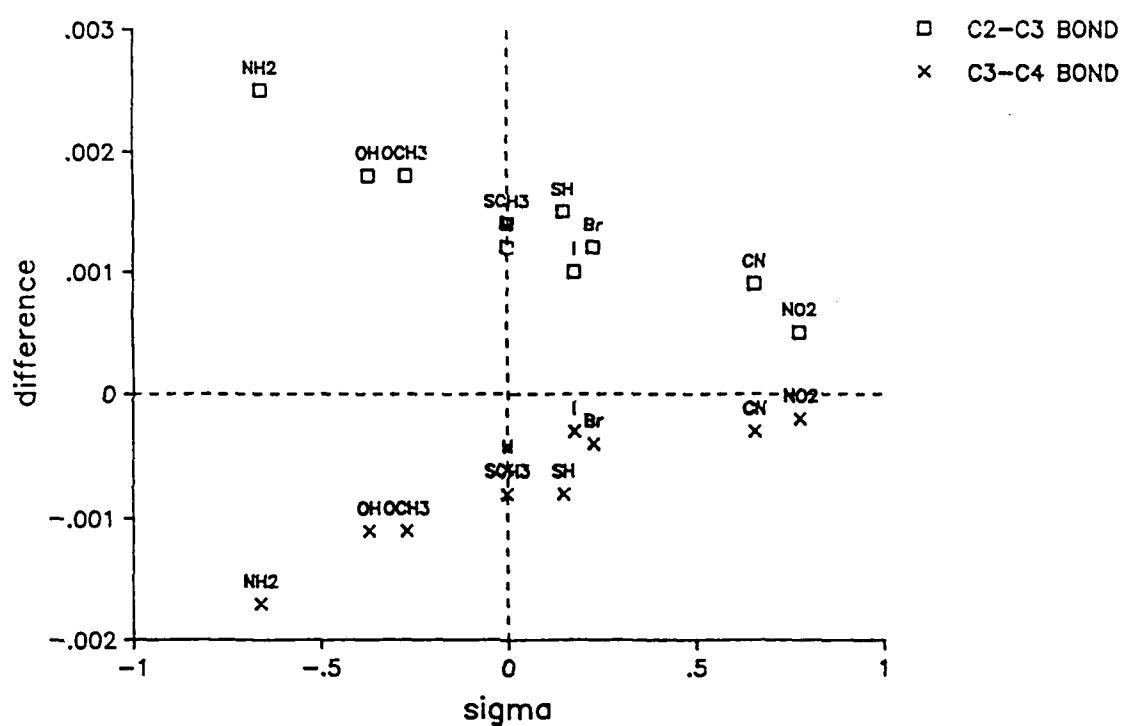


Figure 21. The effect of  $\sigma$  values on the change in C2-C3 and C3-C4 bond distances of p-substituted nitrobenzenes as the NO<sub>2</sub> group is rotated 90 degrees out of the plane of the ring.

# C2-C3 BOND DISTANCE vs SIGMA in meta-substituted nitrobenzenes

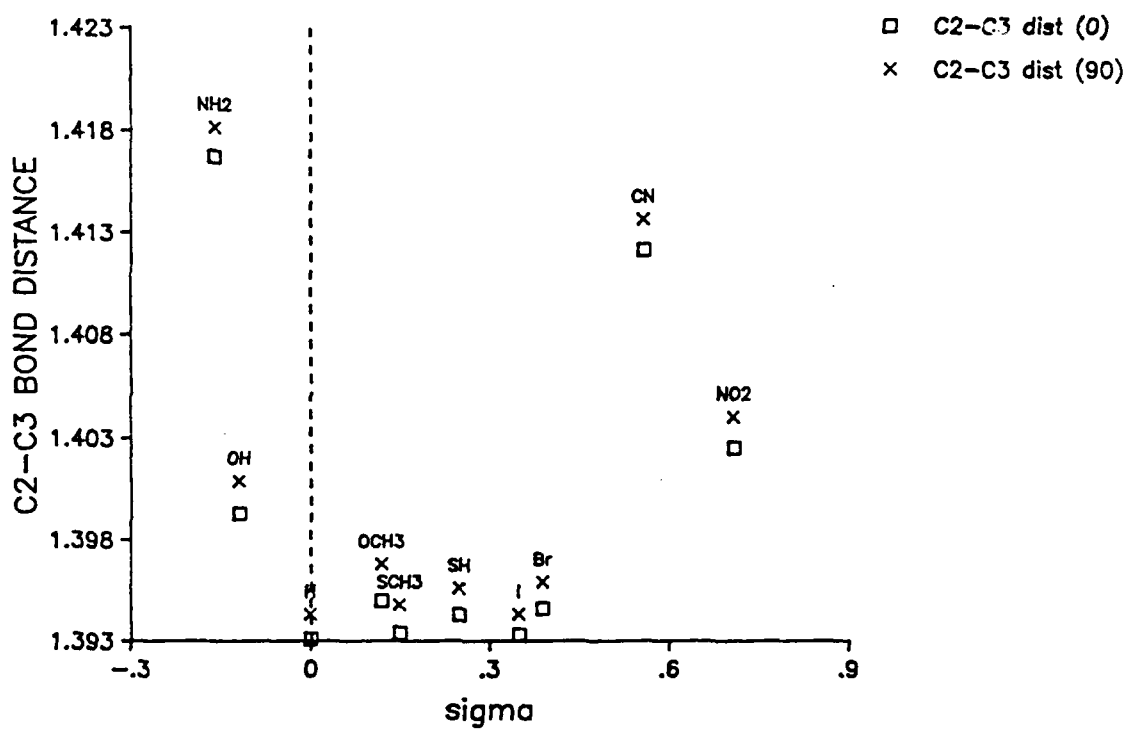


Figure 22. The effect of  $\sigma$  values on the C2-C3 bond distances of the 0 and 90 degree conformers of *m*-substituted nitrobenzenes.

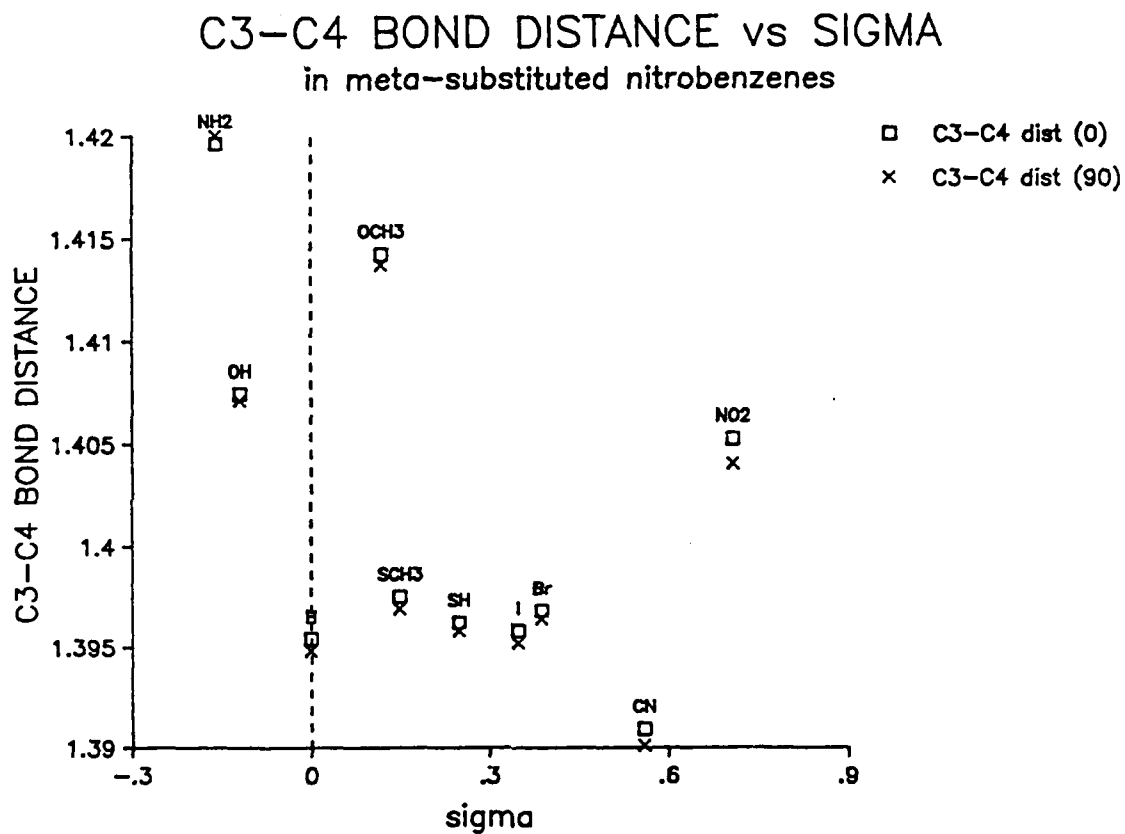


Figure 23. The effect of  $\sigma$  values on the C3-C4 bond distances of the 0 and 90 degree conformers of m-substituted nitrobenzenes.

# DIFF. IN C2-C3 AND C3-C4 BOND DISTANCES in m-substituted nitrobenzenes

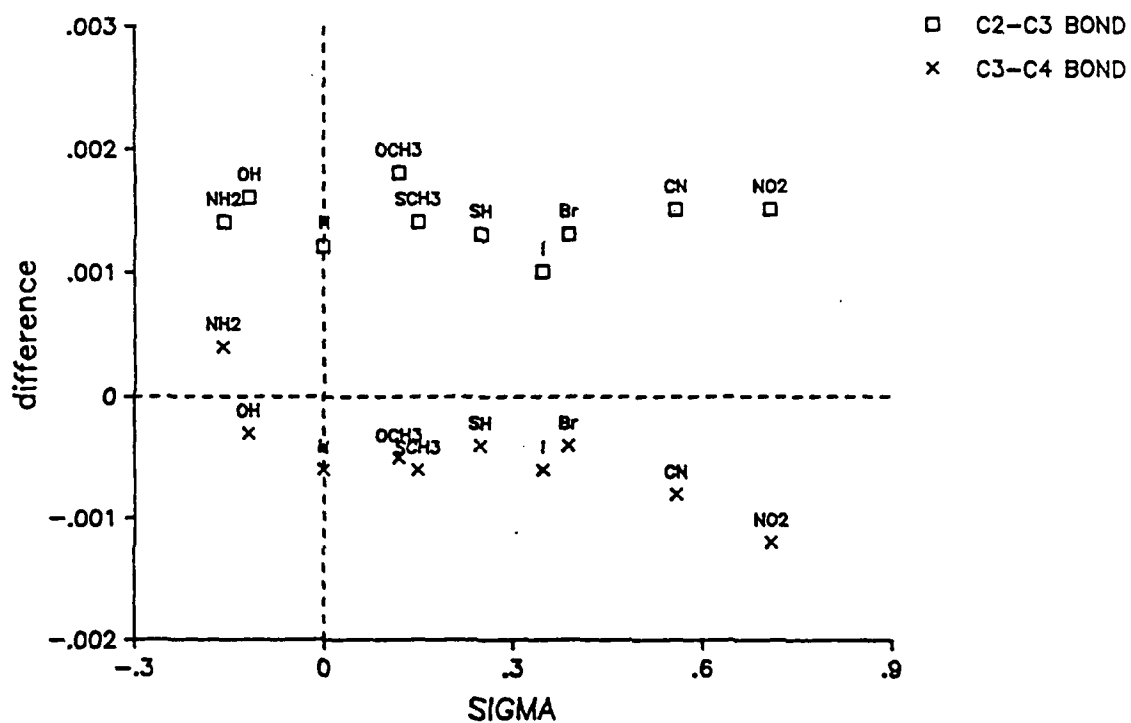


Figure 24. The effect of  $\sigma$  values on the change in C2-C3 and C3-C4 bond distances of m-substituted nitrobenzenes as the NO<sub>2</sub> group is rotated 90 degrees out of the plane of the ring.

# DIFF. IN C2-C3 AND C3-C4 BOND DISTANCES in p-substituted benzoates

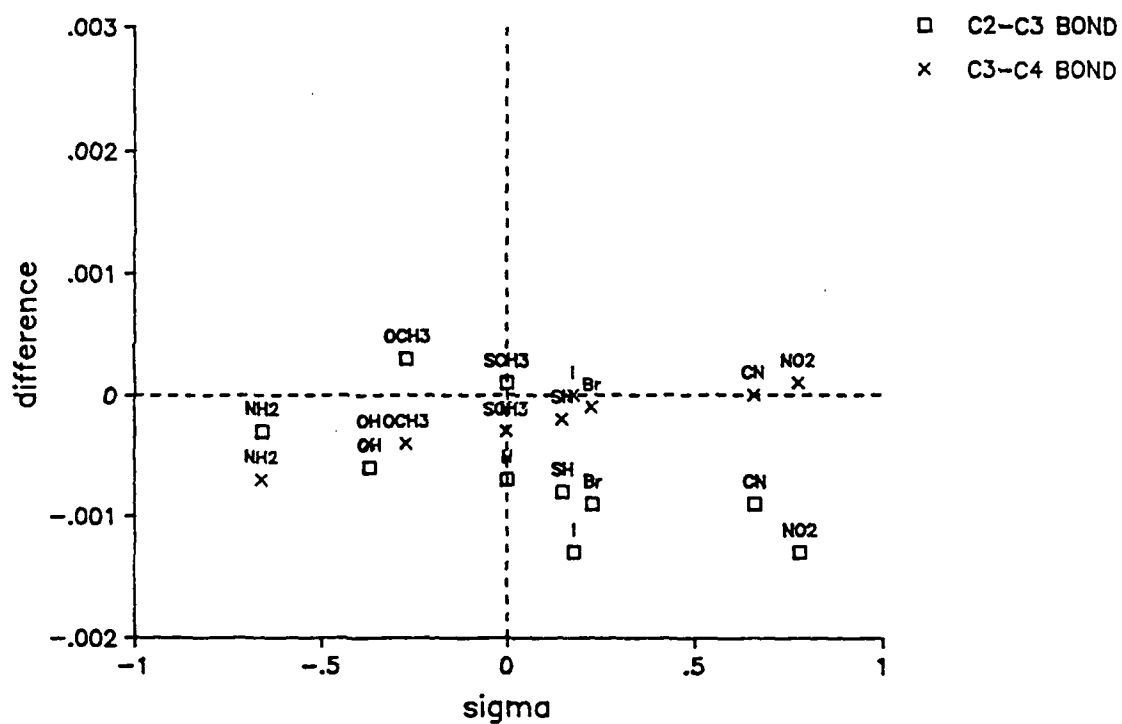


Figure 25. The effect of  $\sigma$  values on the change in C2-C3 and C3-C4 bond distances of p-substituted benzoates as the COO<sup>-</sup> group is rotated 90 degrees out of the plane of the ring.

# DIFF. IN C2-C3 AND C3-C4 BOND DISTANCES in p-substituted benzaldehydes

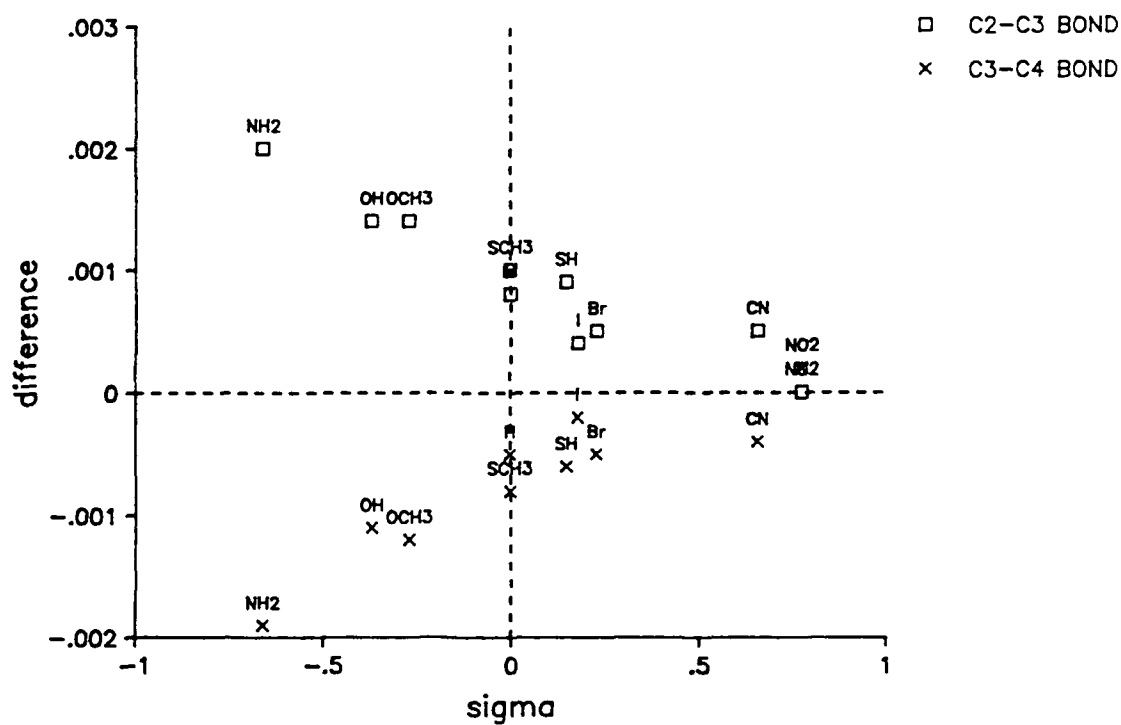


Figure 26. The effect of  $\sigma$  values on the change in C2-C3 and C3-C4 bond distances of p-substituted benzaldehydes as the CHO group is rotated 90 degrees out of the plane of the ring.

% DIFFERENCE IN SUBSTITUENT BOND LENGTH  
in p-substituted nitrobenzenes

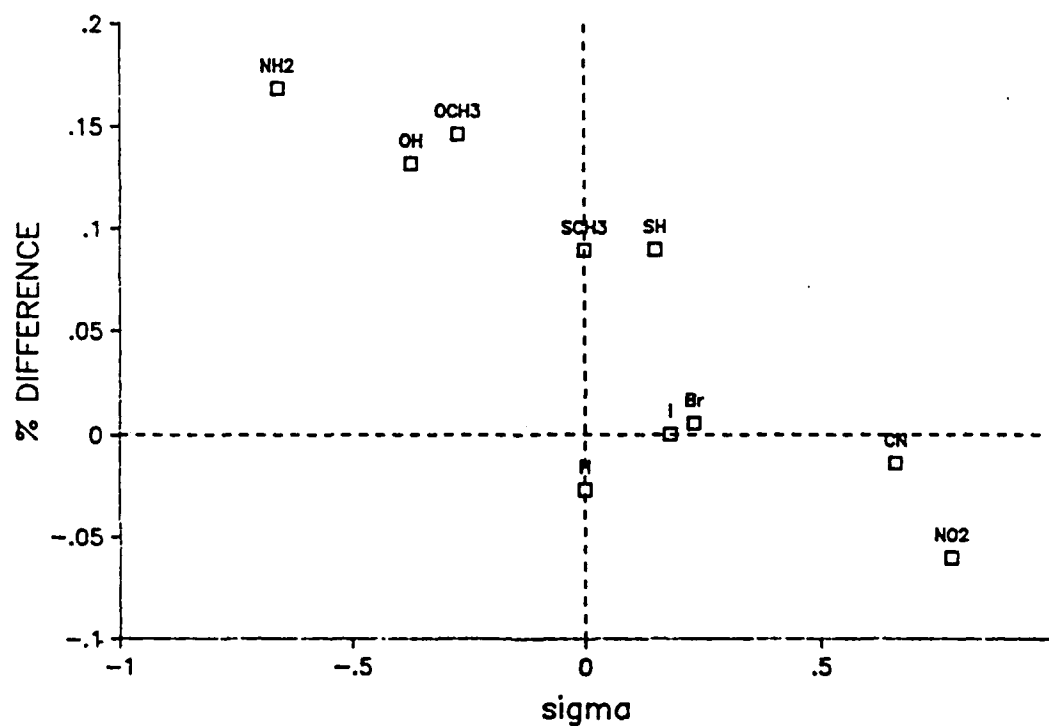


Figure 27. The effect of  $\sigma$  values on the change in C-X bond distances ( $\frac{1}{2}$  change) in p-substituted nitrobenzenes as the NO<sub>2</sub> group is rotated 90 degrees out of the plane of the ring.

% DIFFERENCE IN SUBSTITUENT BOND LENGTH  
in meta-substituted nitrobenzenes

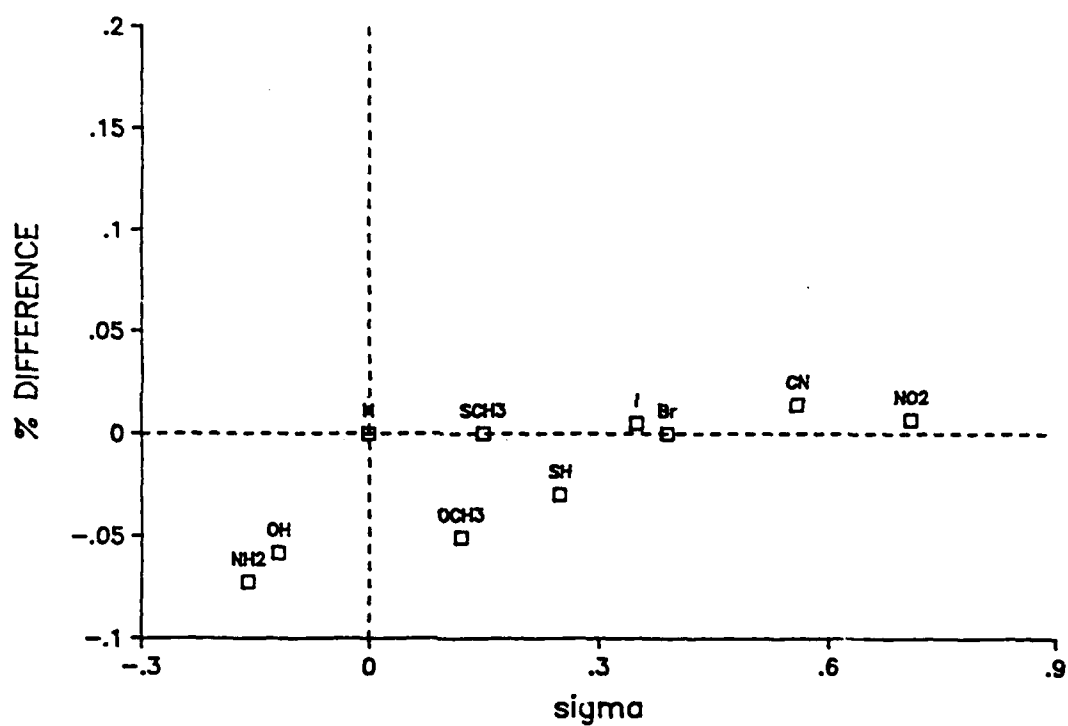


Figure 28. The effect of  $\sigma$  values on the change in C-X bond distances (% change) in m-substituted nitrobenzenes as the NO<sub>2</sub> group is rotated 90 degrees out of the plane of the ring.

# % DIFFERENCE IN SUBSTITUENT BOND LENGTH in p-substituted benzoates

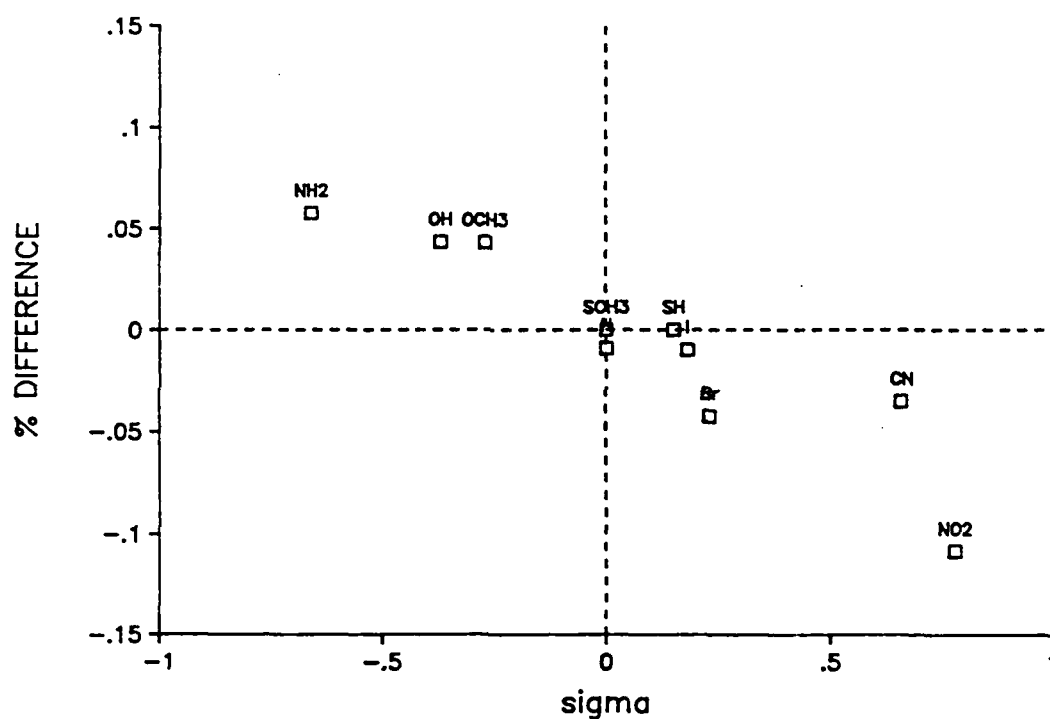


Figure 29. The effect of  $\sigma$  values on the change in C-X bond distances ( $\pm$  change) in p-substituted benzoates as the COO<sup>-</sup> group is rotated 90 degrees out of the plane of the ring.

% DIFFERENCE IN SUBSTITUENT BOND LENGTH  
in p-substituted benzaldehydes

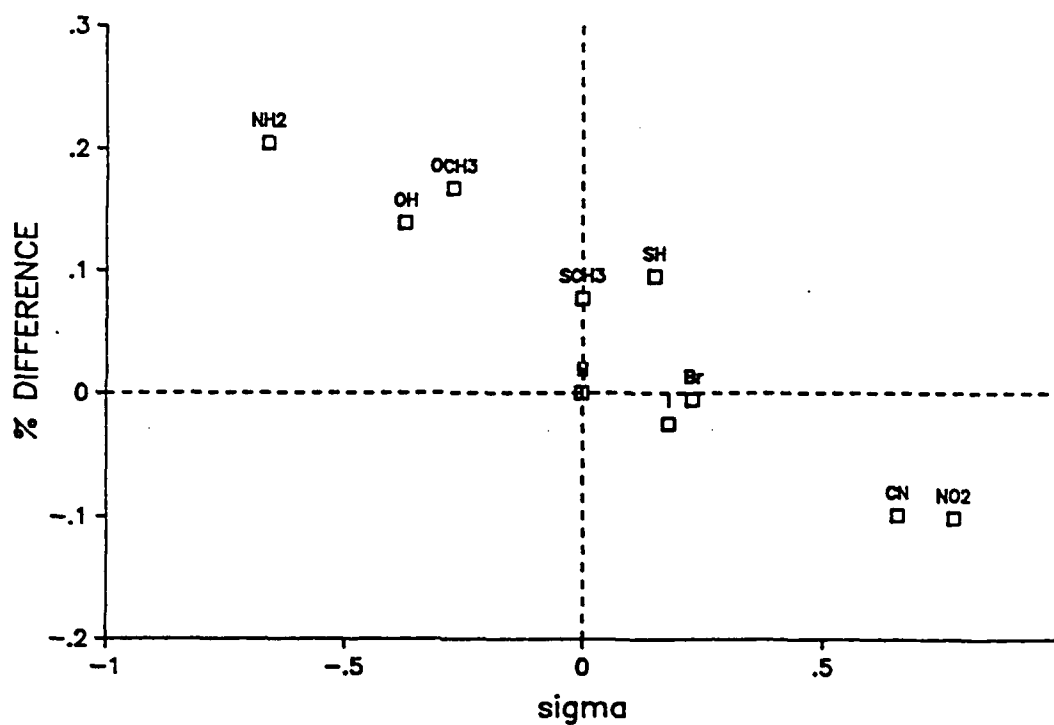


Figure 30. The effect of  $\sigma$  values on the change in C-X bond distances (% change) in p-substituted benzaldehydes as the CHO group is rotated 90 degrees out of the plane of the ring.

# DIFF. IN $p(z)$ ORBITAL OVERLAP vs SIGMA in p-substituted nitrobenzenes

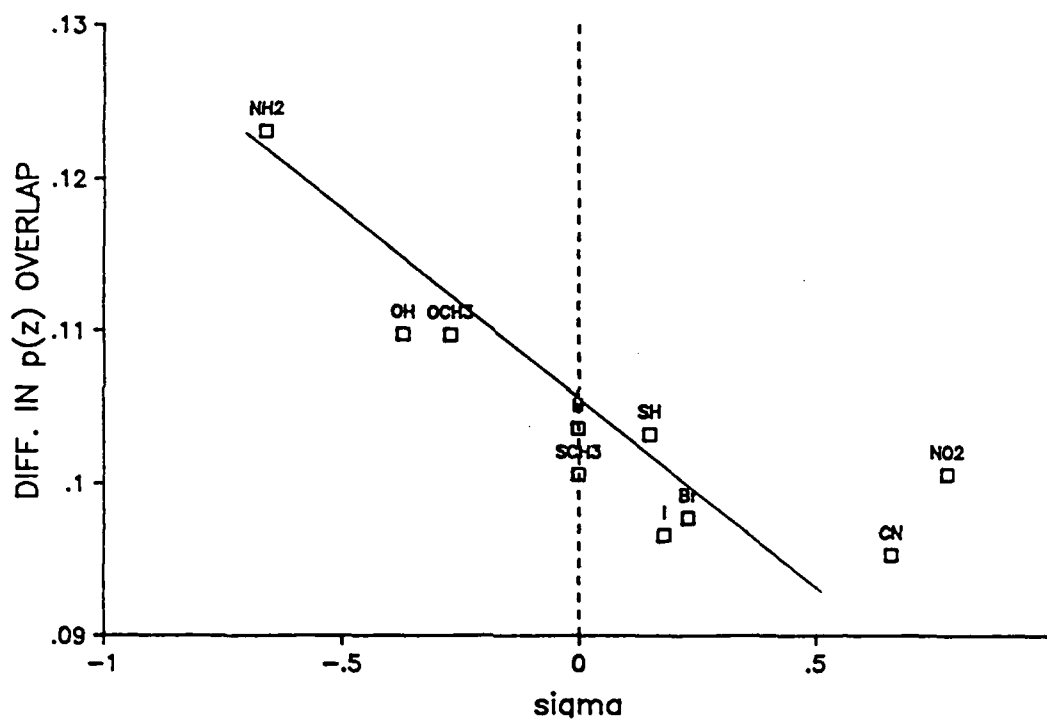


Figure 31. The effect of  $\sigma$  values on the change in  $p(z)$  orbital overlap (density coefficients) between the Cl and N atoms in p-substituted nitrobenzenes as the NO<sub>2</sub> group is rotated 90 degrees out of the plane of the ring. Slope =  $-1.580 \times 10^{-1} \sigma^{-1}$ .

# DIFFERENCE IN $p(z)$ ORBITAL OVERLAP in meta-substituted nitrobenzenes

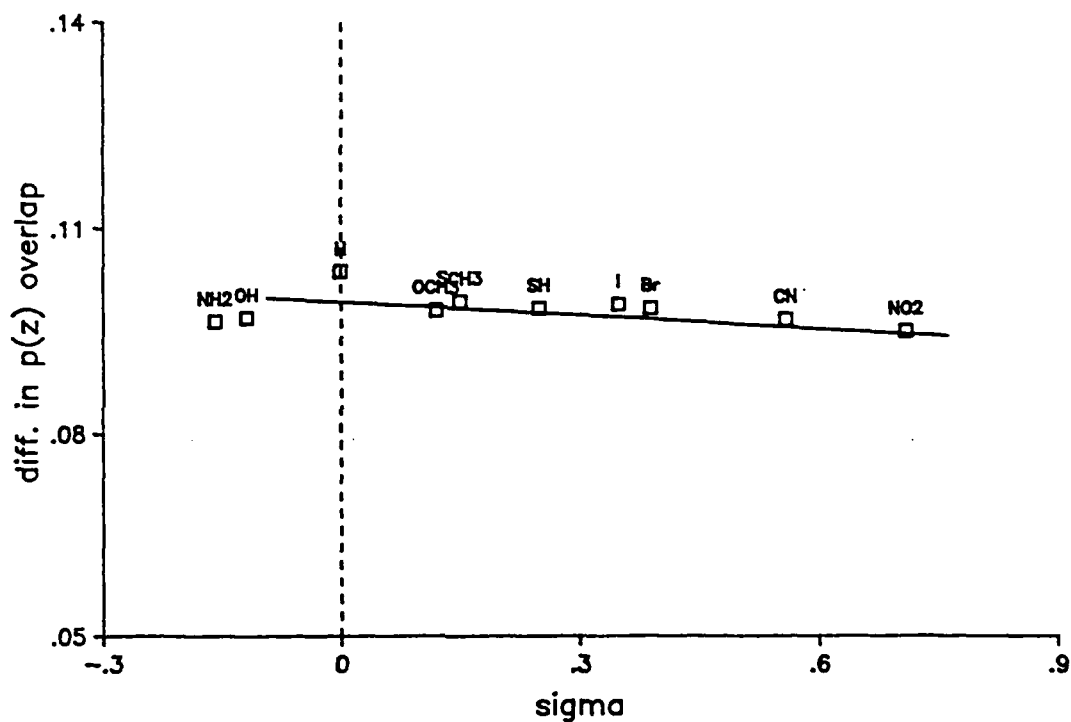


Figure 32. The effect of  $\sigma$  values on the change in  $p(z)$  orbital overlap (density coefficients) between the C1 and N atoms in m-substituted nitrobenzenes as the NO<sub>2</sub> is rotated 90 degrees out of the plane of the ring. Slope =  $-3.106 \times 10^{-3} \sigma^{-1}$ .

# DIFFERENCE IN $p(z)$ ORBITAL OVERLAP in $p$ -substituted benzoates

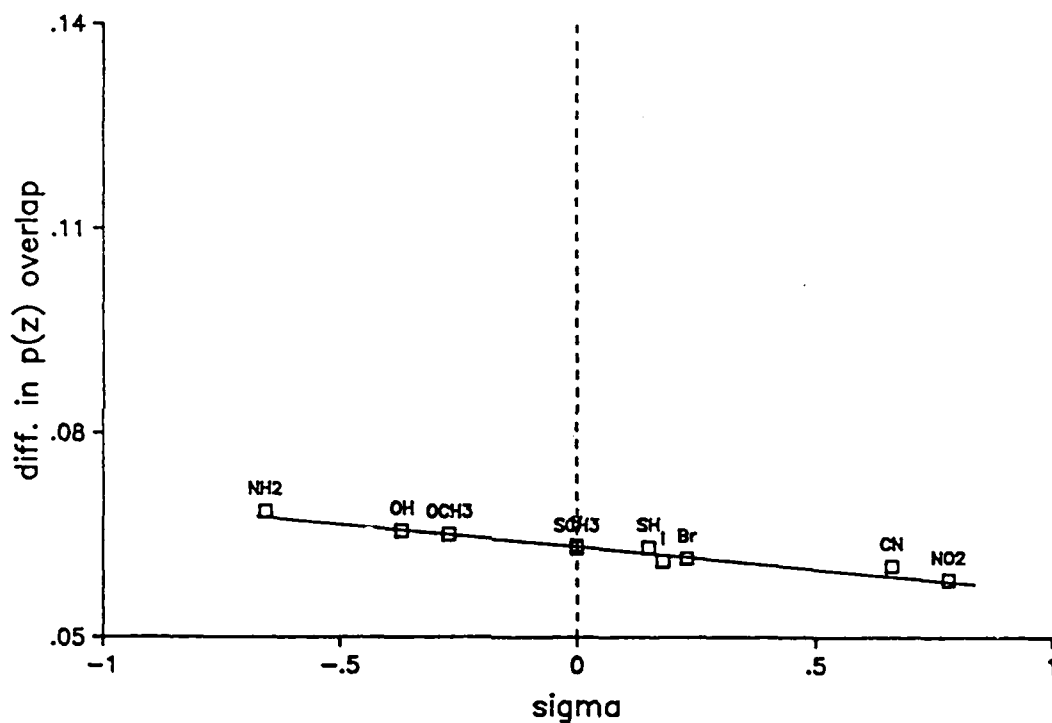


Figure 33. The effect of  $\sigma$  values on the change in  $p(z)$  orbital overlap (density coefficients) between the C1 and C7 atoms in  $p$ -substituted benzoates as the COO' group is rotated 90 degrees out of the plane of the ring. Slope =  $-2.488 \times 10^{-3} \sigma^{-1}$ .

# DIFF. IN $p(z)$ ORBITAL OVERLAP vs SIGMA in p-substituted benzaldehydes

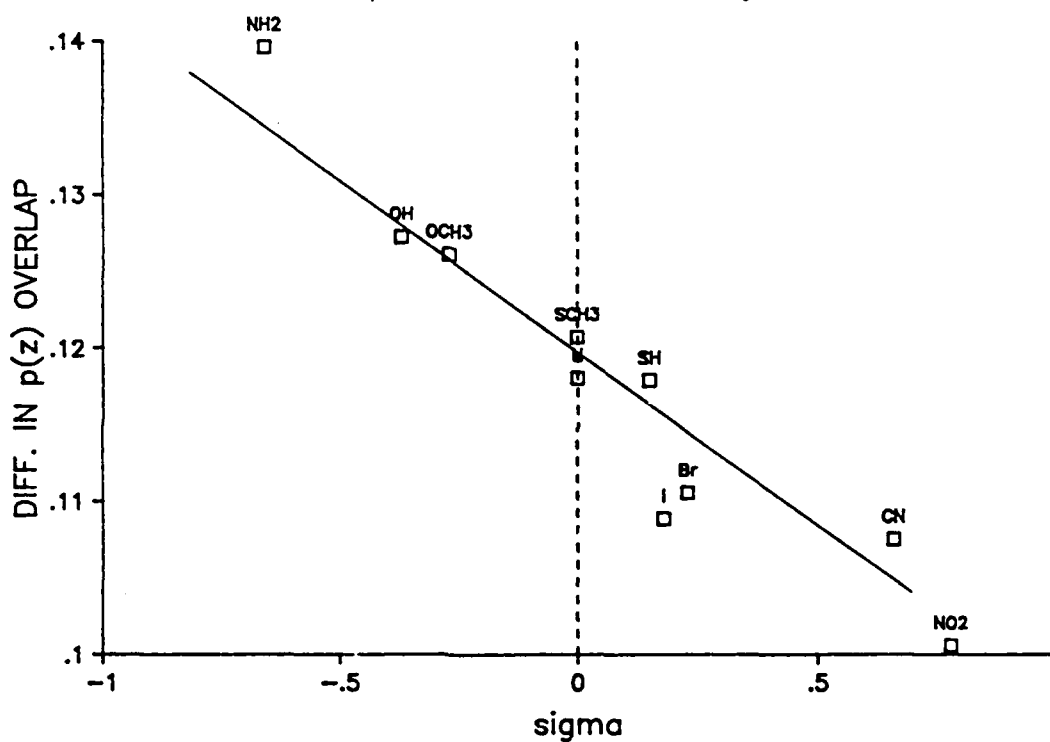


Figure 34. The effect of  $\sigma$  values on the change in  $p(z)$  orbital overlap (density coefficients) between the C1 and C7 atoms in p-substituted benzaldehydes as the CHO group is rotated 90 degrees out of the plane of the ring. Slope =  $-2.488 \times 10^{-3} \sigma^{-1}$ .

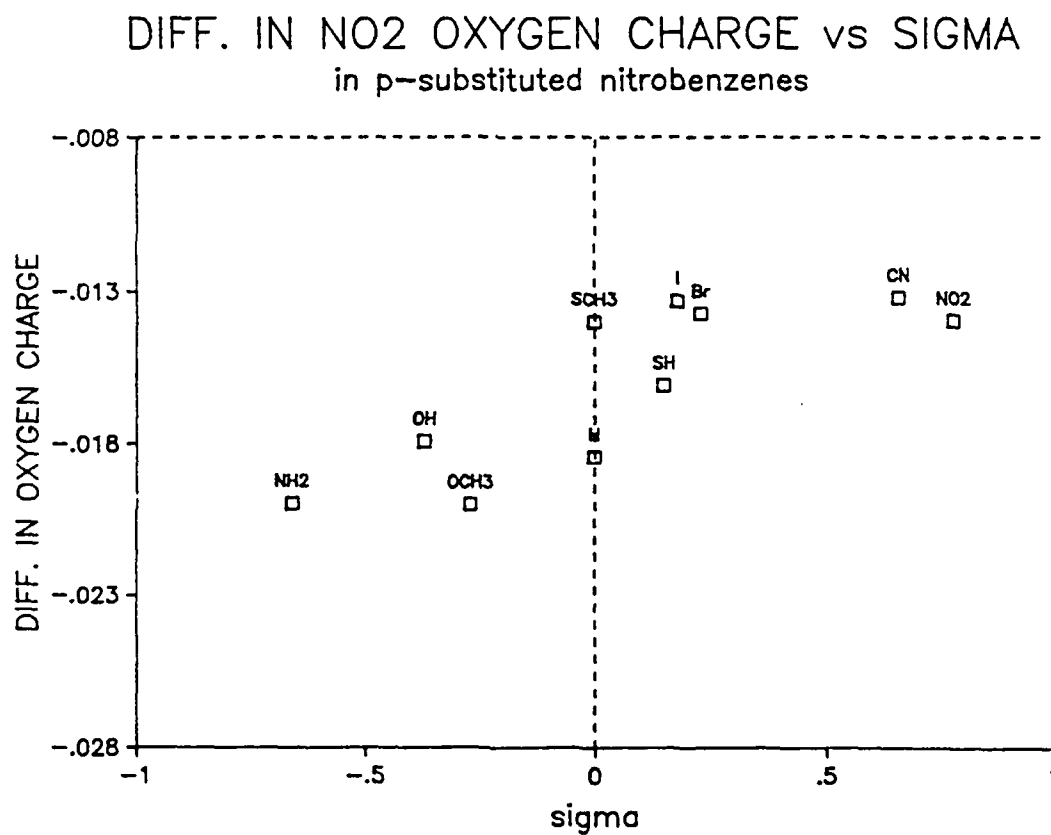


Figure 35. The effect of  $\sigma$  on the change in the total charge residing on the NO<sub>2</sub> oxygens of p-substituted nitrobenzenes as the NO<sub>2</sub> group is rotated 90 degrees out of the plane of the ring.

# DIFFERENCE IN TOTAL CHARGE ON OXYGEN in meta-substituted nitrobenzenes

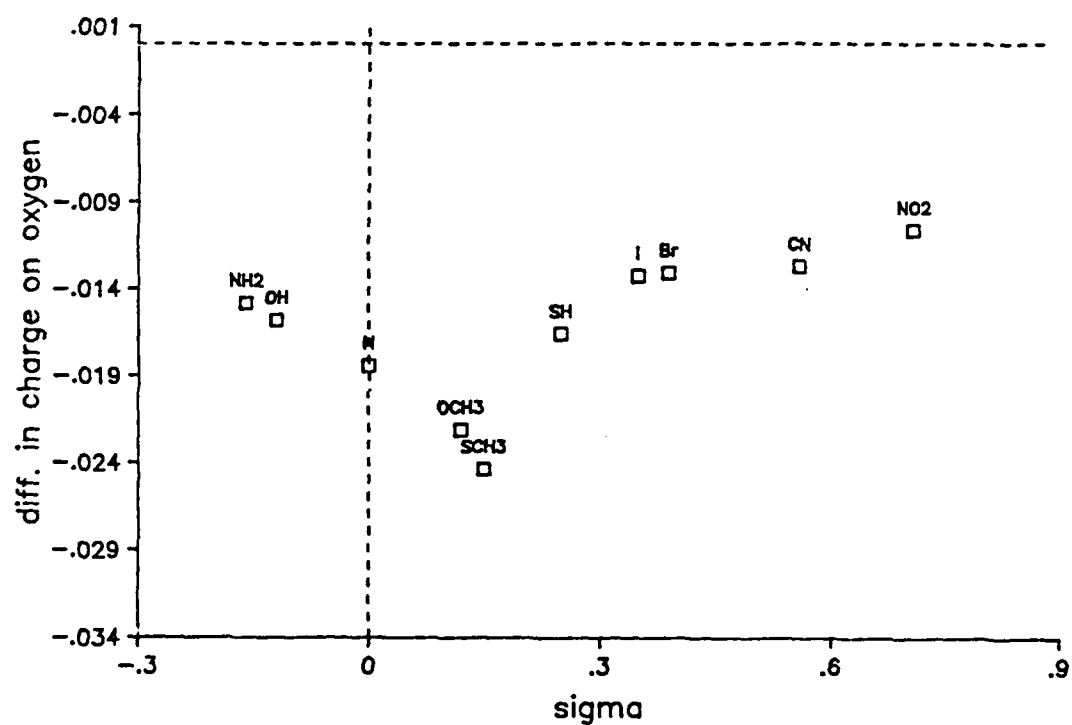


Figure 36. The effect of  $\sigma$  on the change in the total charge residing on the NO<sub>2</sub> oxygens of *m*-substituted nitrobenzenes as the NO<sub>2</sub> group is rotated 90 degrees out of the plane of the ring.

# DIFFERENCE IN TOTAL CHARGE ON OXYGEN in p-substituted benzoates

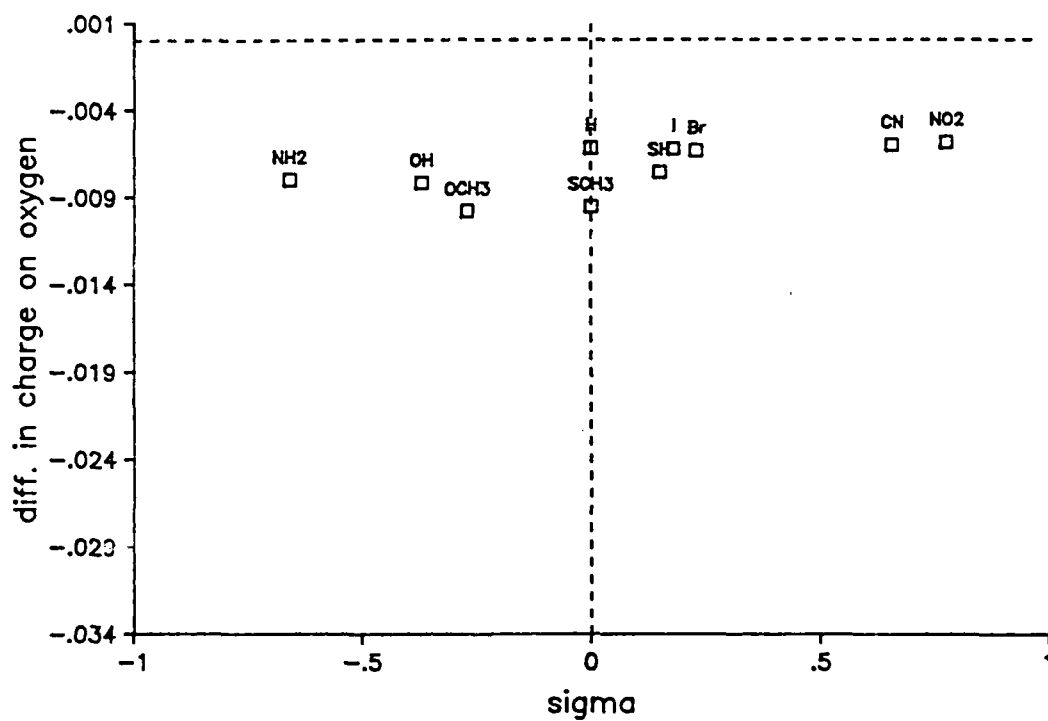


Figure 37. The effect of  $\sigma$  on the change in the total charge residing on the COO<sup>-</sup> oxygens of p-substituted benzoates as the COO<sup>-</sup> group is rotated 90 degrees out of the plane of the ring.

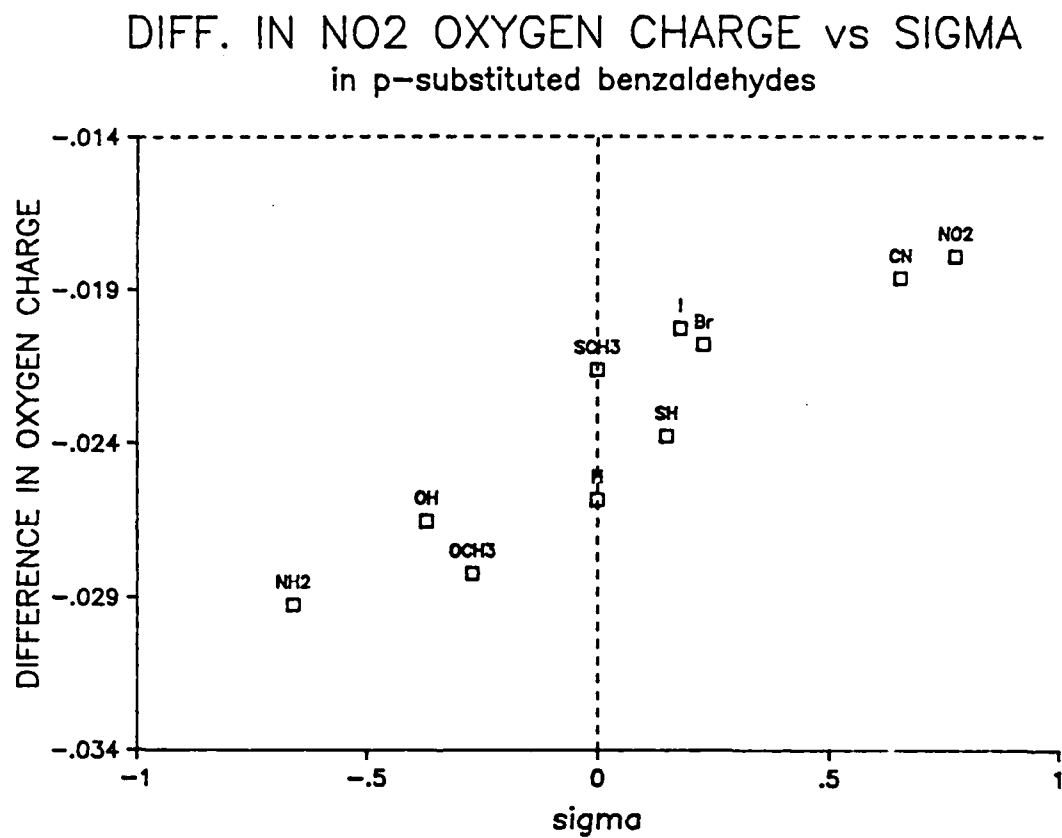


Figure 38. The effect of  $\sigma$  on the change in the total charge residing on the CHO oxygen of p-substituted benzaldehydes as the CHO group is rotated 90 degrees out of the plane of the ring.

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